THE PROCEEDINGS OF THE PHYSICAL SOCIETY

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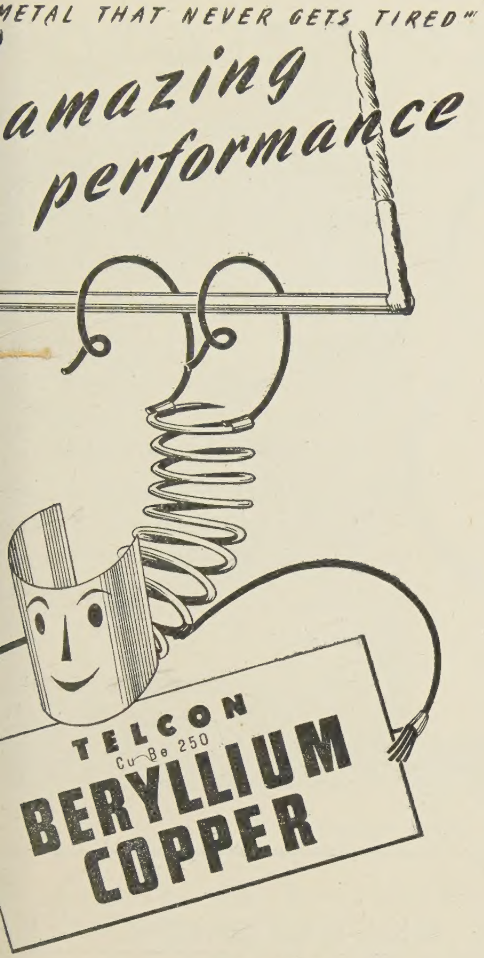

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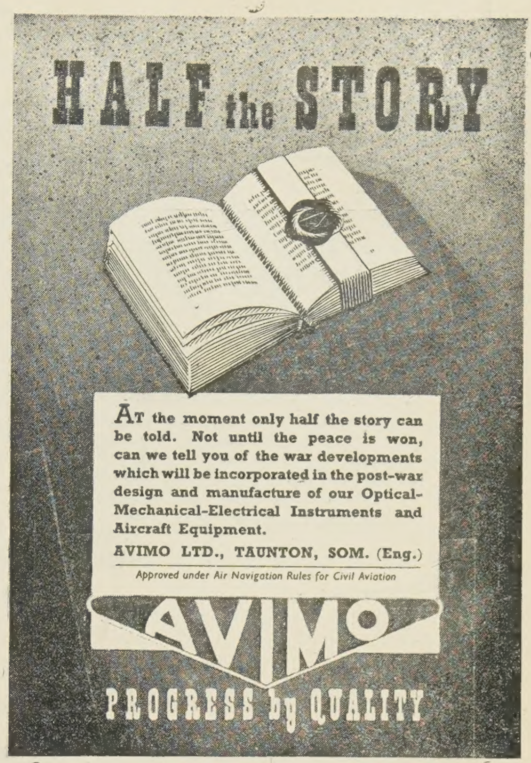

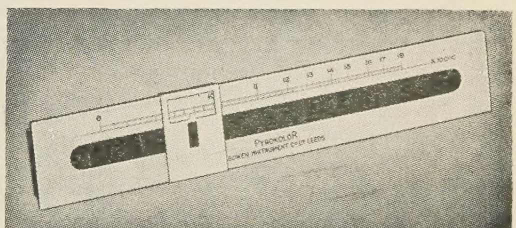

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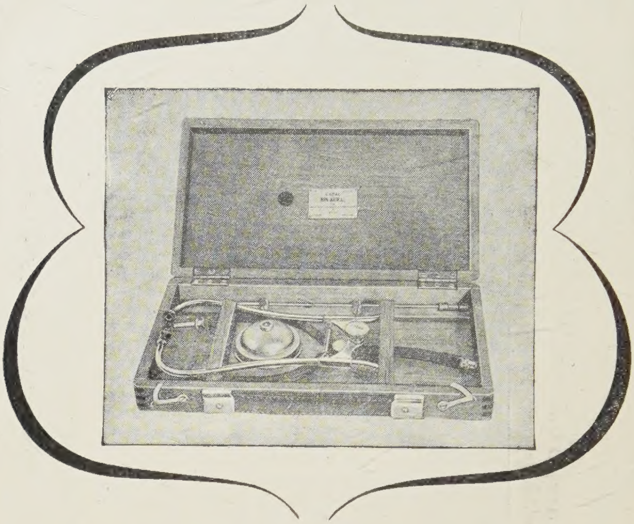

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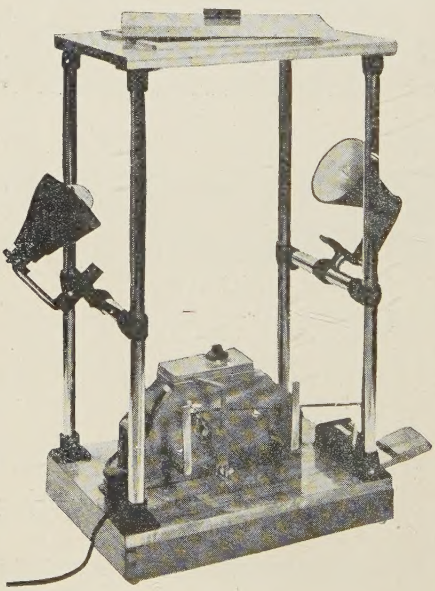

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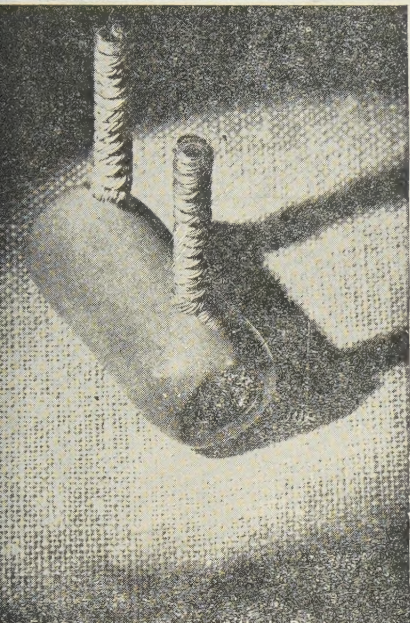
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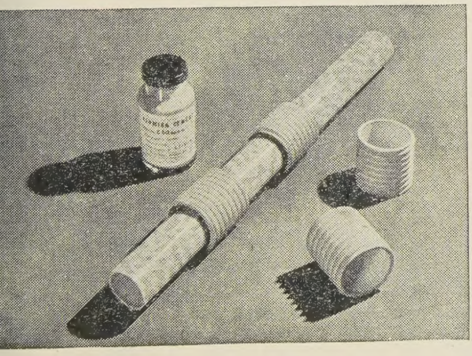

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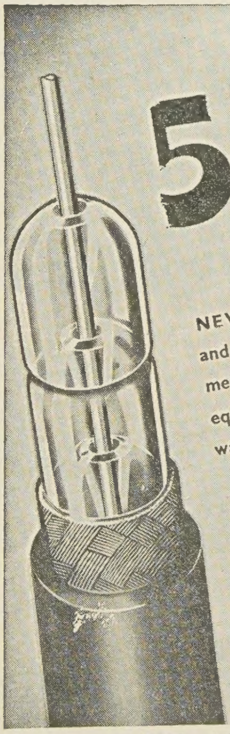

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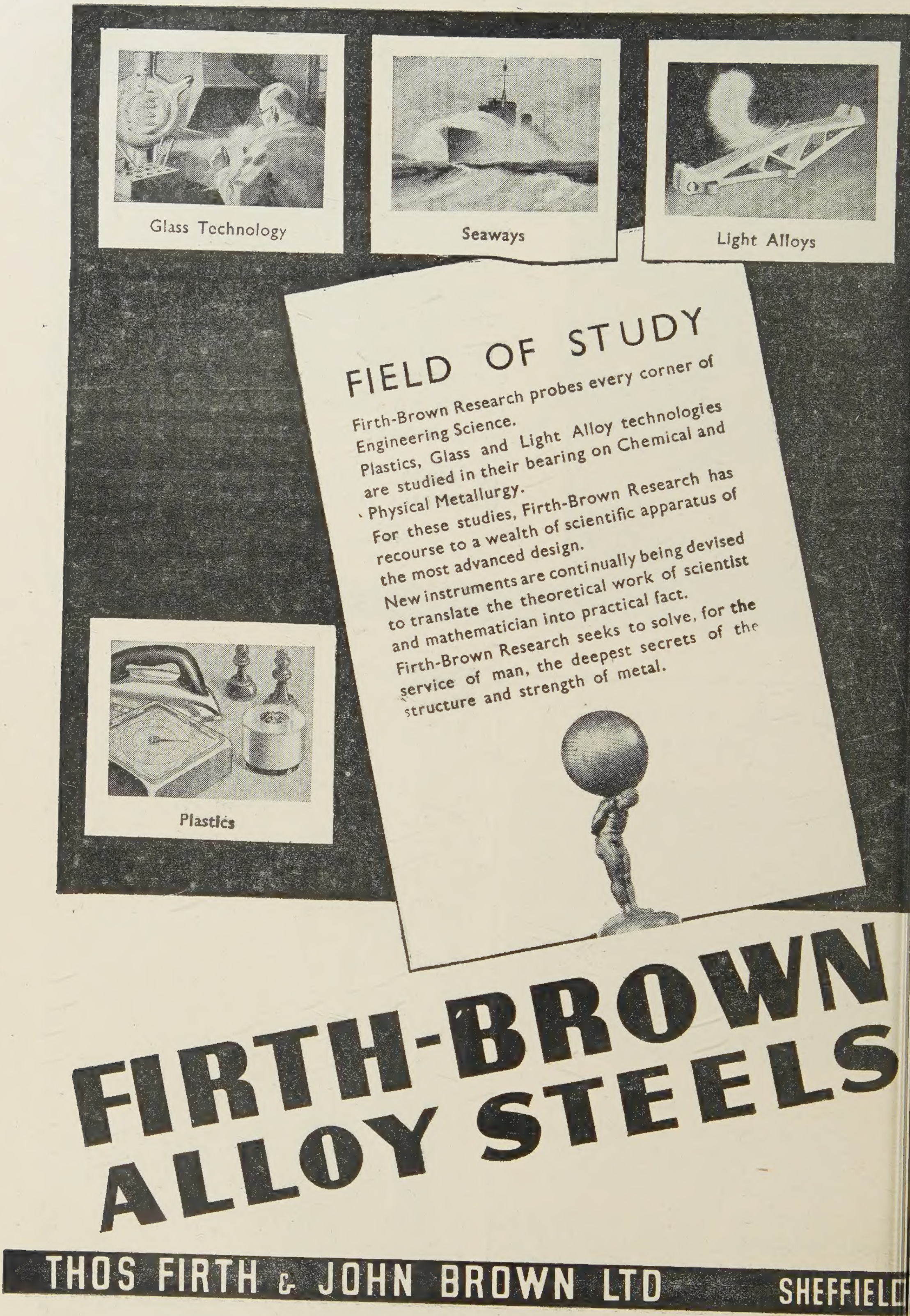

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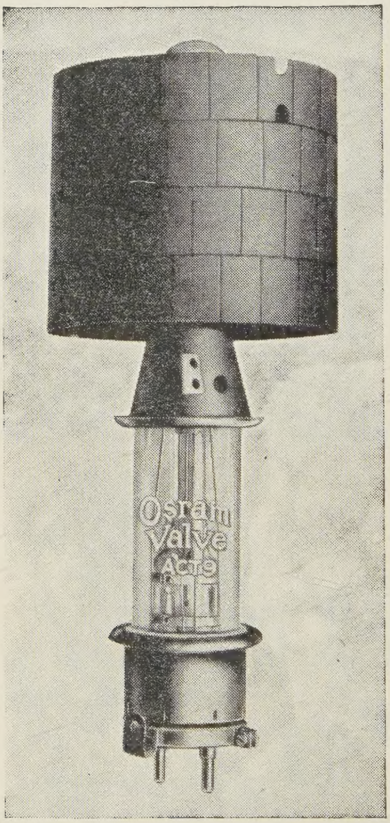

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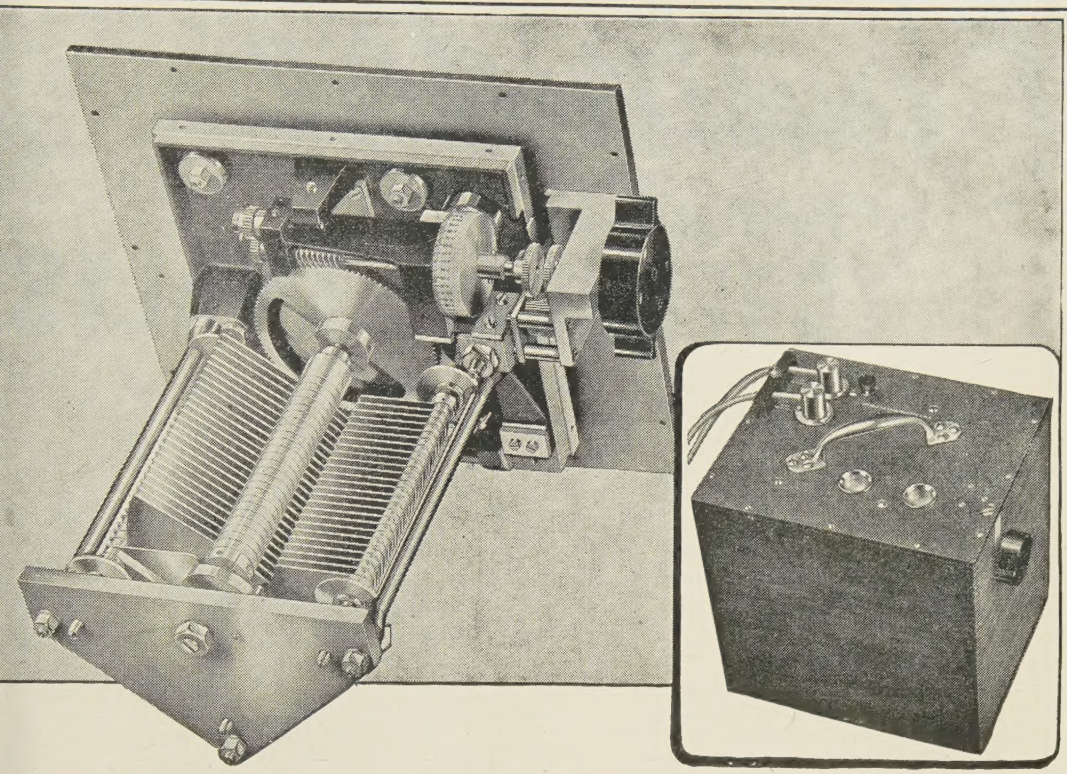

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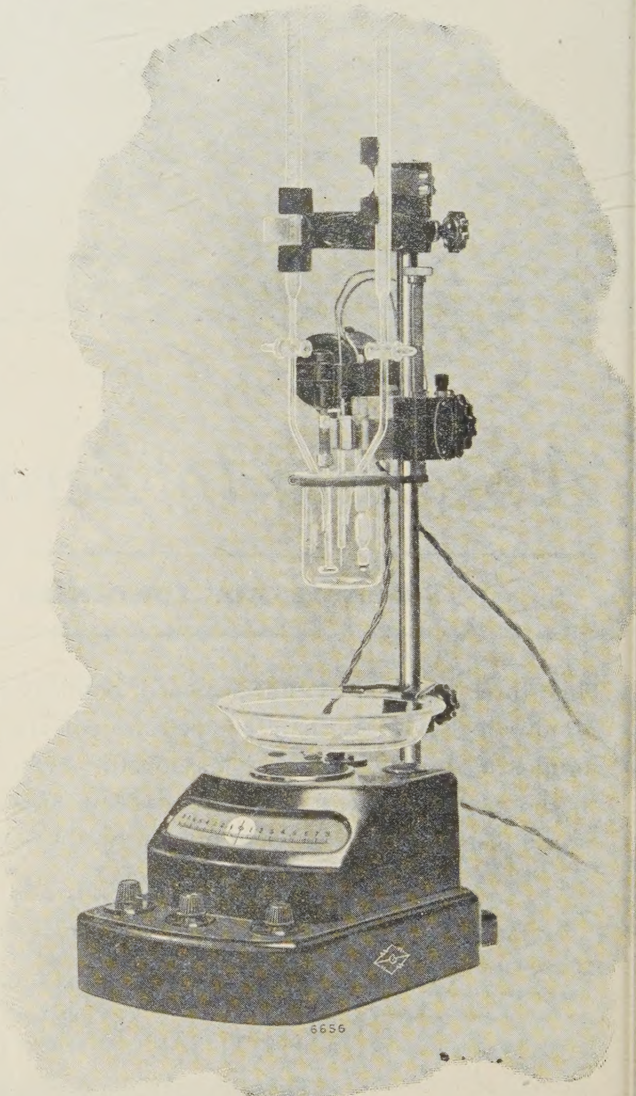

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THE INTERNAL RESISTANCE OF THE SELENIUM RECTIFIER PHOTOCELL, WITH SPECIAL REFERENCE TO THE SPUTTERED METAL FILM

BY J. S. PRESTON AND G. W. GORDON SMITH,
National Physical Laboratory, Teddington

MS. received 13 *September* 1944

ABSTRACT. This paper describes the effect of the internal resistance (other than the barrier-layer) of the selenium rectifier photocell upon its observed characteristics. Methods of measuring the resistance of the selenium layer are cited. This resistance is of the order of 10 ohms in most modern cells. A method of measuring the resistance of the sputtered film is also described. This method is based on measurements, on unlacquered cells, of the distribution of potential over the film resulting from the flow of photocurrent across it when the cell is exposed to a steady uniform illumination. The results obtained with four cells tested gave values between 100 and 600 ohm.cm. for the resistivity of the film. They suggest that for a cell of normal type the value is in the region of 100–300 ohm.cm., while a value exceeding 500 or 600 ohm.cm. is likely to be associated with non-uniformity of the film over the area of the cell, and less satisfactory performance at high values of illumination.

The experiments were made on cells of a production type supplied by a regular maker.

§1. INTRODUCTION

THE selenium rectifier photocell consists of a metal back-plate, usually of iron, coated on one side with a thin layer of light-sensitive crystalline selenium, on the front surface of which a very thin translucent metal film has been deposited, usually by cathodic sputtering. This film may be composed of a noble metal, but its exact nature in the commercial product is not ascertainable. While the cell is exposed to light it will maintain a current in an external circuit connecting the film to the back-plate, the only source of energy being the incident radiation itself. The photocurrent, regarded as a negative electron current, flows through the circuit from film to back-plate, so that the former is the negative electrode of the cell, and the latter is the positive. To facilitate electrical connection to the film, a narrow strip of fusible metal, called the contact strip, or ring, is sprayed on to the film near the periphery of the cell. The surface of the finished cell is usually lacquered to protect it from moisture and mechanical damage. The action of this type of photocell has been studied theoretically, but the studies have generally failed to give quantitative results in good accord with the measured characteristics. In part, this has been due to lack of knowledge of simple features of the cell, such as the resistance of its various elements, which are not easy to determine and may be subject to variation from cell to

cell. The present paper, dealing with the " ohmic " part of the cell resistance as distinct from the barrier layer, is therefore based principally upon experimental considerations. The object of the paper is to examine, simply, the influence of the internal resistance on the behaviour of the cell, and to form some estimate of the magnitude of this resistance. Particular attention is paid to the sputtered film, as it is believed that its resistance has not previously been measured *in situ* by a simple method such as is described below.

§ 2. THE ACTION OF THE CELL

While it is not proposed here to deal with the physical theory of the cell, it will be useful to have in mind a simple picture of its action. The primary action can be considered to be the liberation of electrons from the sensitive selenium layer by the incident light, the number liberated being proportional to the illumination. These electrons, in virtue of their being liberated with a certain initial energy, tend to accumulate on the sputtered film and charge it negatively, in spite of the opposing electric field so created. If there is no external connection between the film and the selenium layer, the film reaches a steady negative potential such that the flow of the photo-electrons on to it is just balanced by an internal back-leakage from the film to the selenium. The net current output of the cell is in this case clearly zero. If, however, an external circuit be connected to the cell, an extra return path for the electrons, from the film to the selenium, is provided. This reduces the potential difference between the film and the underlying selenium, and in consequence of the smaller opposing field, more of the primary photo-electrons flow into the film, within the cell, while fewer leak back. The inflow then exceeds the back-leakage, and the excess of the former over the latter provides the current in the external circuit. The lower we make the external resistance the lower we make the potential difference between film and selenium, i.e., the field opposing the collection of photo-electrons by the film, and so the greater becomes the current-yield of the cell for a given illumination.

Generally, for circuit resistances below a few hundred ohms, the resistance has little effect on the current output for a given (moderate) illumination. Almost all the primary photoelectric current then presumably flows into the external circuit, the opposing field within the cell being too small to cause appreciable back-leakage—or loss of sensitivity, as we may regard back-leakage.

We shall next proceed to a simple analysis of the action just outlined, showing how the internal as well as the external resistance plays a part in determining the potential difference between film and selenium, and so, also, the current output of the cell.

§ 3. THE RÔLE OF INTERNAL RESISTANCE IN THE BEHAVIOUR OF THE CELL

In the simple cell circuit mentioned above there are three parts, namely, (1) the interface or barrier layer, having rectifying properties, and assumed to be the seat of the conversion of radiant into electrical energy; (2) the remainder of the current path in the cell, having a resistance R_I; and (3) the external circuit

having a resistance R_E. Now if V be the voltage developed at the interface and i be the current flowing, we can at once write $V=i(R_I+R_E)$. We shall assume that V is the most important physical factor in this equation and that the higher the voltage V which the interface is called on to generate, the lower will be the sensitivity of the cell (defined as the ratio of the current to the incident illumination). It is seen that this is consistent with well-known experimental results. For instance, if we keep the circuit resistance constant and increase the current (by raising the illumination), or if we raise the circuit resistance and keep the current constant (by suitable adjustment of the illumination), or if we raise both circuit resistance and current output, the sensitivity is found to diminish. Our equation shows that in all three cases V has been increased. (It may be noticed here that the term iR_E on the R.H.S. of the equation is the voltage across the terminals of the cell).

For a proper insight into the behaviour of the cell, then, some knowledge of V is requisite. This at once involves R_I, although, of course, when R_E is large enough, it may often prove permissible to take the terminal voltage iR_E as a sufficiently good approximation to V, and neglect the term iR_I altogether. Even then, however, we must have some idea of the order of R_I at least, in order to know whether it is permissible to neglect it. At the other extreme, when the cell is short-circuited (or virtually so, as in the Campbell-Freeth circuit) and R_E is zero, R_I is the influential factor. We then have $V=iR_I$, and we see, for instance, that short-circuiting the cell does not make V (and so also the cell sensitivity) entirely independent of i, the current drawn from the cell. Short-circuiting the cell clearly reduces the range of variation of V, and with it the variation in sensitivity, for a given range of i, but it does not eliminate these variations altogether. (In other words, short-circuiting the cell results in better, but not exact, " linearity ".)

The picture of the selenium photocell just given is admittedly incomplete, but it serves to show the importance of the rôle played by the internal resistance, and, together with knowledge of the approximate value, or even the order of this resistance, it forms an adequate basis for very useful working rules in the use of the cells. For example, we may wish, for convenience in making certain observations, to assume that the cell sensitivity is constant, and to determine what conditions must be observed in order that the error resulting from this assumption shall not exceed a specified amount. We might then determine in the most convenient way (e.g. with R_E large and R_I certainly negligible by comparison) the appropriate value of V which must not be exceeded. Then, if we also know R_I roughly, we can insert the values of V and R_I in the simple equation given above, and so determine sufficiently closely for practical purposes the related ranges within which we must confine i and R_E.

§4. THE NATURE OF THE RESISTIVE ELEMENTS OF THE CELL

The purpose of this paper, in addition to drawing attention to the part played by the internal resistance in the behaviour of the cell, is to provide information on which a rough estimate of R_I for a typical cell can, if desired, be based, and to sketch the methods by which this information can be obtained for any given cell. We notice now, therefore, that the internal resistance comprises two

parts, namely, that of the selenium layer and that of the sputtered film. Methods of measuring the former are well known and are briefly referred to below. For the latter, a method is described which is believed to be sound and at the same time simple. Before describing these methods, however, an important point relating to the film must be referred to. We have so far assumed implicitly that V is uniform over the surface of the cell. Strictly, this assumption is not valid, for the resistance of the sputtered film leads to a non-uniformity in V. We ought, correctly, to apply the equation for V to each element of surface, rather than to the cell as a whole. R_I would then apply to a particular element under consideration, and the part of it due to the metal film only would clearly be smaller for elements near the contact strip than for remoter ones. This dependence of R_I for an element of surface, upon the location of the element, results in a variation of V over the surface of the cell. The variation may be large if either the resistivity of the sputtered film, or the current drawn from the cell, be unusually large. The consequences of such a case will be discussed later, for it is upon the variation of V over the cell surface that the present work is based.

§ 5. METHODS OF MEASURING THE RESISTANCE OF THE SELENIUM LAYER

As we have seen, the internal resistance of the cell, represented above by R_I, consists of two parts, namely, the resistance of the selenium layer and that of the sputtered film. The effective resistance of either will of course depend upon the current distribution in it. In the case of the selenium layer we may assume a uniform current distribution in almost all cases, since the sensitivity is generally uniform over the surface.

At the cost of destroying the cell it is possible to measure the resistance of the layer alone. For this purpose a comparatively heavy layer of fusible metal is sprayed on to the surface of the unlacquered cell, over the sputtered film, so as to form an upper electrode of negligible resistance. The cell in this condition will still have the properties of a rectifier. The effect of the interface having rectifying properties can, however, be eliminated by a well-known method. This consists in measuring the current passing through the cell for various values of voltage applied, in the "conducting" direction, from an external source. As the current is increased the differential of the current with regard to the voltage tends to a definite limit, while the resistance offered by the interface tends to zero. The limiting value of the differential is thus the resistance required. A close approximation to the limiting value can generally be obtained with applied voltages of 2 volts or less. Various investigators have used this method, and their results indicate that the resistance of the selenium layer in a cell of average size, say 45 mm. diameter, is generally of the order of 10 ohms.

A similar method might be applied to the cell in its original state, and expected to give a result representative of the total "ohmic" resistance of the cell, including that of the thin film, under normal conditions of use. It would not do so, however, because, as we shall see later, the resistance of the film is relatively high, so that if an external voltage were applied between the back-plate and the contact strip, there would be a concentration of current in the immediate neigh-

bourhood of the strip. Such a current distribution is quite unlike that of the photocurrent when the cell is used in the ordinary way. This method has sometimes been used in the past without recognition of its shortcomings.

§6. MEASUREMENT OF THE RESISTIVITY OF THE FILM

It is possible, however, to measure the resistivity of the sputtered film alone. The method is based on the above-mentioned variation of V over the surface of the cell. The cell is exposed to a fairly high illumination and the variation in potential over the film is explored.* It is possible, with simple assumptions and for cells of simple shape, to relate the potential at any point on the film to the co-ordinates of that point, the film resistivity, and the photocurrent generated per unit area of the surface.

Consider for instance a rectangular photocell ABCD (figure 1), with the contact strips along the edges AB, CD. Assume that the properties of the sputtered film, and also the cell sensitivity, are uniform over the surface. Then, if the cell be uniformly illuminated, the current flow over the film will be symmetrical with regard to the centre line drawn parallel to AB, CD. The electron current will, in fact, flow everywhere away from the centre line, and in a

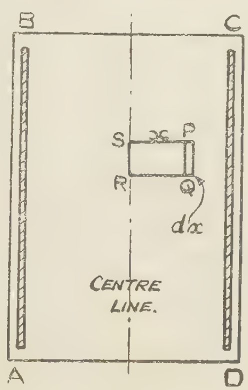

Figure 1.

direction at right angles to it. Thus, all the current arising within a rectangular transverse area PQRS, where RS is along the centre line, will flow across PQ. Now let PQ be of unit length, and SP be x. Also let c be the photocurrent generated per unit area of the surface, and R the resistance, between two opposite sides, of a square of film of side unity. Consider then the small rectangular element of film whose longer dimension is PQ and shorter one dx. The current flowing across this element will be the current generated within PQRS, which is cx. The resistance of the element, in the direction of the current flow, will be Rdx. Hence the potential difference dp, across the element, will be $cRxdx$. If p be the potential difference between points on the line PQ and the centre line we have by integration

$$p = cRx^2/2. \qquad \ldots\ldots(1)$$

* Unlacquered cells are necessary. Specimens were kindly supplied by Messrs. Evans Electroselenium, Ltd., to which firm due acknowledgment is made.

(For a circular cell with an annular contact strip, the corresponding relation is easily seen to be $p=cRr^2/4$, where r is the distance from the centre of the cell.)

We may test whether a relation of this form holds for a given cell, and if it does we can measure p, c and x, and so deduce R. The value of c is of course obtained as the quotient of the total photocurrent by the effective sensitive area. The following account describes the details of such a test.

A rectangular cell was mounted upon the movable system of a travelling microscope so as to be capable of movement in its own plane in a direction at right angles to the two contact strips (figure 2). A probe, made of fine springy

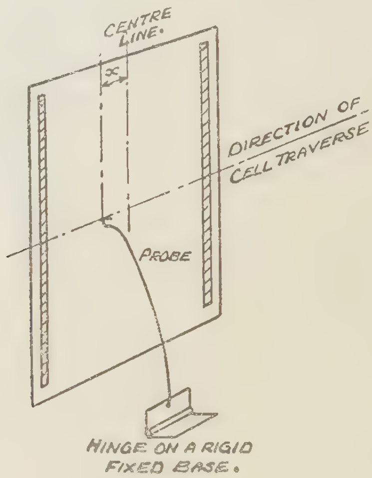

Figure 2.

wire, with the end turned back on a small radius, so as to give a smooth point of contact, was mounted on a hinge fixed on the stationary frame of the microscope. The probe could thus be brought into contact with the cell, or removed at will while the position of the cell was being changed, without uncertainty as to the relative positions of the cell and probe. The micrometer screw of the microscope movement was used to vary, and to measure accurately, the position of the cell relative to the probe, and contact with the cell surface was thus possible at any desired point on a transverse line across the cell. The central transverse line was, in fact, chosen so as to avoid possible "end-effects". The cell was exposed to a steady uniform illumination, and by the means just described, readings of the potential of the cell surface were made on the transverse line, at points spaced 2 mm. apart. A potentiometer method was employed, so that no current flowed into or out of the cell, via the probe, at the moment of measurement. Instead of measuring the potential difference, p, between the probe and the centre of the cell, at which no permanent form of contact could easily be provided, measurements were made between the probe and a conductor connecting the two contact strips together, values of p being obtained as differences. The conductor joining the contact strips was also connected to the negative terminal of a 15-ohm micro-ammeter whose positive terminal was connected to the back-plate. This instrument measured the total photocurrent.

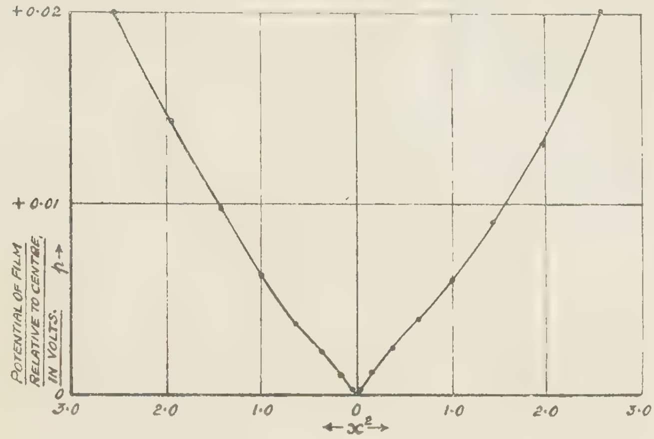

Figure 3. Square of distance from centre line, in cm²

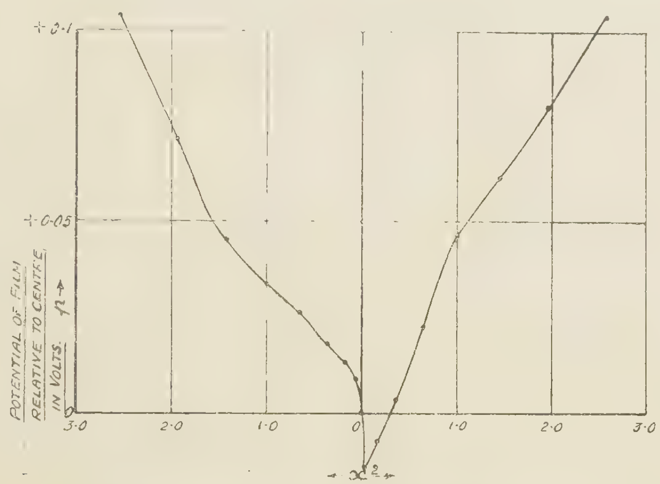

Figure 4. Square of distance from centre line, in cm²

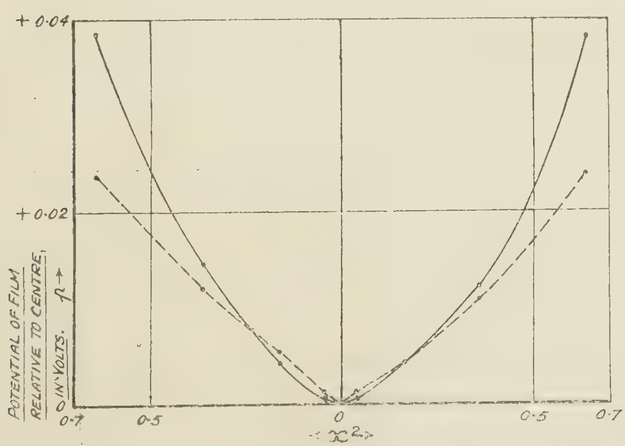

Figure 5. Square of distance from centre line, in cm²

Care was taken that the illumination was uniform over a sufficient area, and that the total photocurrent was maintained constant for any one set of readings corresponding to a complete traverse of the cell.

§7. RESULTS

The curves shown in figures 3, 4 and 5 show some typical results. The corresponding data are given in table 1. Readings were taken in every case for several different values of the total photocurrent less than those stated, but the resulting curves were all of the same shape as those shown. The values of p observed at any particular point on the cell were, in fact, proportional to the total photocurrent, to within a few per cent.

Cells nos. 1 and 3 were of regular production types, while nos. 2 and 4 were sputtered with rather thinner films as a matter of interest. The higher sensitivities of the latter are consistent with a smaller light-absorption in the film. For the measurement of sensitivity the illumination was 10 f.c. and the resistance of the microammeter was 10 ohms. The light source had a colour temperature of 2848° K.

Table 1

Cell no.	Cell size (mm.)	Sensitive area (cm^2)	Sensitivity * (μA./f.c.)	Total current (mA.)	Current per unit area (μA./cm^2)	Potential diff. centre to edge (volts)
1. (Fig. 3)	37×50	15·0	7·0	2·0	133	0·0201
2. (Fig. 4)	37×50	15·0	7·3	2·0	133	0·104
3. (Fig. 5 broken curve)	22×40	5·9	2·8	1·5	254	0·0238
4. (Fig. 5 full curve)	22×40	5·9	3·0	1·5	254	0·0385

(* refers to the unlacquered cell.)

In the case of cell no. 2 the observed relation between p and x^2 departs considerably from the linear form. The possible reasons for this are discussed later. For cells nos. 1 and 3 the relation approximates fairly closely to the linear form, while the results for no. 4 are intermediate. We shall for the present

Table 2

Cell no.	x^2 (cm^2)	p (volts)	c (A./cm^2)	R (ohm.cm.)
1	2·56	0·0201	$1{\cdot}33 \,.\, 10^{-4}$	118
2	2·56	0·104	$1{\cdot}33 \,.\, 10^{-4}$	611
3	0·64	0·0238	$2{\cdot}54 \,.\, 10^{-4}$	293
4	0·64	0·0385	$2{\cdot}54 \,.\, 10^{-4}$	474

disregard the departure from linearity and calculate the value of R in each case from equation (1) by inserting the value of p corresponding to the potential difference between the centre and the contact strips or edge of the cell and the value of x^2 for the half-width of the cell. This will presumably give a rough average value of R in cases where the film is non-uniform. Table 2 shows the values of resistivity so obtained.

§8. DISCUSSION OF RESULTS

The results indicate that the resistivity of the sputtered film, for an average normal cell, lies in the region 100–300 ohm.cm. Cells with a thinner film than usual had a resistivity of 500 or 600 ohm.cm. These had a higher sensitivity (table 1), at least at an illumination of 10 foot-candles, no doubt because the thinner film absorbs less light. It is seen, however, that the film resistivity must be made two or three times higher than usual in order to secure so small an increase in sensitivity as 7 %. (It is, of course, well known that for very thin sputtered films the resistance decreases very rapidly with increase in thickness, while the transmission factor falls only slightly over the same range in thickness.)

Consider now the curves showing the observed values of p. These can be regarded as curves showing the variation of V over the surface of the cell (though the ordinates are not actual values of V, since V includes any potential drop in the selenium layer and also the terminal voltage). Figure 4 (cell no. 2), then, illustrates a case where the value of V at the centre of the cell must be at least 0·1 volt greater (arithmetically) than the value at the edge. So that even if the cell were short-circuited, and the peripheral regions were called on to furnish only a small voltage, the central region would be generating a voltage of at least 0·1 volt. This difference in V between the centre and the edge of the film is associated with the passage of the photocurrent through the film on its way to the contact strip. The difference is, of course, greater the greater the film resistivity, and increases with the photocurrent. It is easy to see, then, that when a cell having a poor film of unusually high resistance is called on to furnish a large photocurrent, V may tend to reach a value much exceeding 0·1 volt near the centre of the cell. Now for most commercial cells a rather marked fall in sensitivity sets in for values of V in excess of about 0·1 volt, while for cells of poor quality the critical value of V may be much lower than this. In the conditions just considered, therefore, the sensitivity of the central regions of the cell will be considerably lower than that of regions near the contact strip—that is to say, the sensitivity of the cell as a whole will be lower than it would be for much smaller photocurrents, for which V nowhere reaches such a high value.

Hence, too thin a film may be detrimental to the sensitivity of the cell as a whole at high illuminations, though it may result in a higher sensitivity than usual at low illuminations because of its comparatively high optical transmission. This is presumably one reason why the film on a normal cell is, as we have seen, made a little thicker than is necessary to give maximum sensitivity in the region of 10 foot-candles illumination. Sensitivity at low illuminations is not, for these reasons at least, a reliable measure of the general "goodness" of a cell.

It has frequently been suggested that, in order to avoid the conditions in which the film might be damaged or V become excessive over certain areas of the cell when a large photocurrent is being generated, extra central contact strips might be provided. Such a device is, however, of academic rather than practical interest, for the use of several small cells of standard design, in parallel, provides an equally satisfactory and rather more convenient solution. Probably, also, the variation in potential over the surface of the cell accounts for the peculiarity often observed with cells prepared by those not thoroughly versed in the art, that the sensitive portion appears to be confined mainly to regions near the contact strips. The film resistance in such cells may be abnormally high, and this would result in a serious reduction in sensitivity per unit area in the central regions, even for quite small values of the photocurrent. Moreover, as we have seen, in a poorly made cell the critical value of V may be much lower than 0·1 volt, and so the effect of a high film resistance would be further accentuated.

Let us now discuss the possible reasons for the observed departure from linearity of the relation between p and x^2 in the case of cells such as nos. 2 and 4. It may arise from non-uniformity in the sensitivity of the *selenium* over the surface of the cells. Now we might well suppose that a cell which shows good uniformity does so because the maximum possible sensitivity has been secured for every element of the surface. If so, its overall sensitivity must be higher than that of a non-uniform cell in which by definition the sensitivity cannot everywhere be a maximum. However, the cell having the anomalous characteristic of figure 4 is rather more sensitive than the one to which figure 3 applies, and which certainly exhibits good uniformity. It seems highly improbable therefore that the peculiar shape of the curve in figure 4 arises from non-uniformity in the state of the selenium. A similar argument applies, but with less cogency, to the cells of figure 5.

It is much more likely that the observed departures from the linear relation result from non-uniformity in the resistance of the sputtered films, with a distribution of photocurrent different from the simple one assumed in deriving equation (1). This is in accord with the observation already made that variations in the thickness of a film which have only a very small effect on the amount of light transmitted (and therefore on the sensitivity of the cell) may be associated with large variations in resistance.

The method described above for measuring the resistivity of the sputtered film on a selenium rectifier photocell would seem, then, to be applicable with confidence and to give the desired result to a good order of accuracy. When the sputtered film is non-uniform, this fact is immediately revealed by the method, but an approximate estimate of the average resistivity may still be obtainable. The method stresses the misleading nature of a simplification often made in describing the cell and its mode of action. This simplification is to regard the film, as a whole, as having a certain resistance through which the whole photocurrent flows. To do this is strictly incorrect, though it is often permissible in considering the general behaviour of the cell, as in the earlier part of the present paper. It might be urged that direct measurements of the resistivity of sputtered films deposited on glass, for instance, would have yielded all the information desired. This is not so, for the character of a sputtered film depends on the

material on which it is deposited, so that films sputtered on glass and upon selenium under identical conditions may not be alike in their properties.

§ 9. CONCLUSIONS

We may briefly summarize our investigations into the behaviour of the selenium rectifier cell as follows:—

(1) A simple study of the part played by the internal resistance of the selenium rectifier cell serves to show the main features in its influence on the behaviour of the cell. A knowledge of the approximate value of the internal resistance is useful in this respect, and also as a guide to the experimental conditions appropriate to any practical application. The internal resistance comprises both the resistance of the selenium layer and that of the sputtered film. These two differ in many important ways, and must be considered and measured separately.

(2) The only convenient and valid method of measuring separately the resistance of the selenium layer involves destruction of the cell. Other investigators have obtained values of the order of 10 ohms by this method.

(3) The method now described for measuring separately the resistivity of the sputtered film is based on an exploration of the potential distribution over the film under normal conditions of use. The cell is in no way injured. The distribution is found to be of a type predicted on theoretical grounds. Values of 100 to 300 ohm.cm. are found for the resistivity of the film on cells of a regular production type. Other cells tested gave results of 500 to 600 ohm.cm. for the mean resistivity, with evidence that when the resistivity is as high as this, the film may not be very uniform, and the performance of the cells in certain respects unsatisfactory.

(4) It is correct to regard the cell as being made up of a large number of small elements, the effective film-resistance of each element depending on its position with regard to the contact strip. The simplified picture in which the film is regarded as offering some definite resistance to the photocurrent as a whole is frequently misleading. No value of resistance which might correspond to such a picture is therefore given. A value appropriate to any size of cell and set of conditions may be calculated, however, when this simplification is justifiable.

ACKNOWLEDGMENT

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A NOTE ON THE SPECTRUM OF MgO

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ABSTRACT. Some observations on the spectrum of magnesium burning in air have been made with a grating spectrograph of dispersion $\sim$7·4 A./mm. Wave-length data are given for a weak sequence of bands with head at about 4820 A. and of a complex system in the region 3600–4000 A. from measurements of plates taken in a first and second order respectively. The λ4820 sequence may possibly form part of the well-known green system of MgO. The stronger bands of the near ultra-violet system have also been photographed in absorption.

§ 1. INTRODUCTION

The most prominent features in the spectrum of magnesium burning in air are the well-known band system in the green, a weaker system at longer wave-lengths, a complex series of bands apparently degraded in both directions in the near ultra-violet (3600–4000 A.), and the λ5211 system of MgH, all superimposed on a continuous background of radiation from the incandescent oxide. Although our primary concern has been with other aspects of this spectrum, we have found that the description given in the literature of the green system and of the bands at 3600–4000 A. is inadequate in certain respects. The purpose of this note is to provide some further data which may be of use in any future and more fundamental work.

§ 2. EXPERIMENTAL

Small strips of magnesium ribbon were burned in air and the light focused directly on the slit of a 2·4-m. grating instrument. Most of the observations were made in a first order (linear dispersion about 7·4 A./mm.), but the bands at 3600–4000 A. were also photographed in a second order. Ilford Ordinary and Special Rapid Panchromatic plates were used in the appropriate wave-length regions: they were developed in Ilford Process developer to secure as much contrast as possible.

§ 3. THE GREEN SYSTEM

A reproduction of a grating spectrogram of the green system is given in the plate (*a*). The strongest features are seen to be two sequences of closely-spaced bands degraded to the violet with leading heads at about 5206 A. and 5007 A.: the former is somewhat overlaid by MgH structure. These bands have been measured many times, and the approximate wave-lengths of the earlier members of the two sequences are not in doubt. However, a third, weaker sequence, with head at about 4820 A., is also evident. This sequence was apparently

first observed by Brooks (1909), who gave rough measurements to ± 1 A. The only other measurements known to the authors are from the low-dispersion work of Ghosh, Mahanti and Mukkerjee (1930), although the bands are also to be seen on the reproduction given by Eder (1904). Our figures are given in table 1.

Table 1

λ (I.A.)	$\nu_{vac.}$ (cm.$^{-1}$)
4825·62*	20717·0
18·55	747·4
10·15	783·6
01·57	820·7
4791·24	865·6
80·45	912·7
70·75	955·2

* This band is considerably weaker than the others ; it can scarcely be seen on the reproduction (see plate (*a*)), but seemed rather more definite on the negatives. A band at about this wave-length is listed both by Brooks and by Ghosh, Mahanti and Mukkerjee.

The appearance and occurrence of these bands at once suggest that they represent a third sequence of the green system of MgO, and it is in fact possible to include them in a Deslandres array which numerically is quite feasible. With the λ 5206 band as the 0,0 band, the band at 5007 A. becomes the first member of the 1,0 sequence, and the bands given in table 1 fit satisfactorily into the positions of the 2,0 sequence. This scheme leads to values of the vibration frequencies as follows: $\omega_{\frac{1}{2}}' \sim 760$, $\omega_{\frac{1}{2}}'' \sim 710$ cm.$^{-1}$.

There is a serious objection to this arrangement, however, which is based on the distribution of intensity among the bands. Although most photographic plates show rather sharp changes of sensitivity around 5000 A., it is probable that the sequences do decrease in intensity in the order λ 5007, λ 5206, λ 4820, as indicated in the plate (*a*). On a rough visual intensity scale of 10 we would guess the figures 10, 6 and 1 respectively. The above scheme therefore represents a rather anomalous intensity distribution with the 1,0 band as the strongest. The only comparable distribution in the literature appears to be that given by Meggers (1933) for an infra-red system of CaO ($\nu_0 = 9491$ cm.$^{-1}$). This system consists of three sequences of bands degraded sharply to the violet, and the intensity figures listed are: (0,0) band, intensity 3; (1,0), 30; (2,0), 20. So far as we know, in all other systems arising from states with similar r_e and ω_e values, leading to narrow Condon parabolae, the strongest band is invariably the 0,0 band (see Jevons, 1932).

On intensity grounds, therefore, the present analysis must be regarded as rather improbable. However, the only obvious way of reconciling this analysis with a normal intensity distribution would appear to involve rejection of the λ 5206 band—a procedure for which there is no other justification. In these circumstances it is clear that further work is necessary to decide the nature of the λ 4820 sequence: a search for the isotope effect in the λ 5007 and λ 5206 bands on high dispersion, using a source free from MgH emission, would probably be decisive.

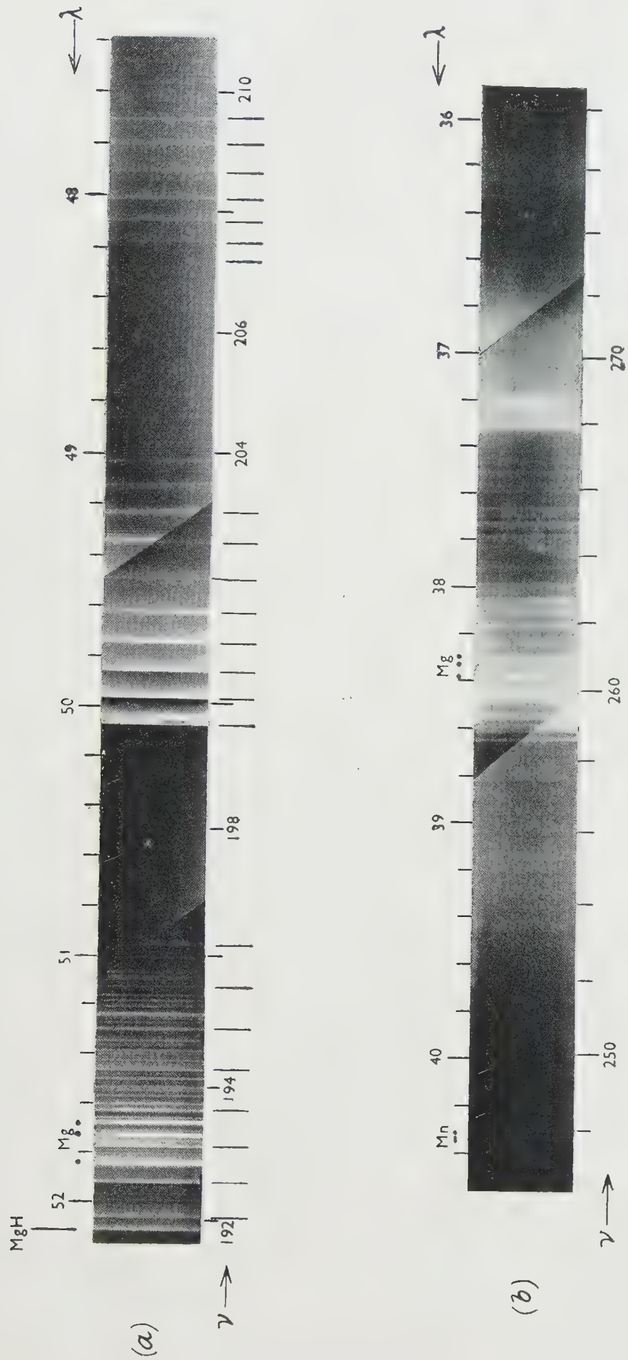
§4. THE ULTRA-VIOLET BANDS

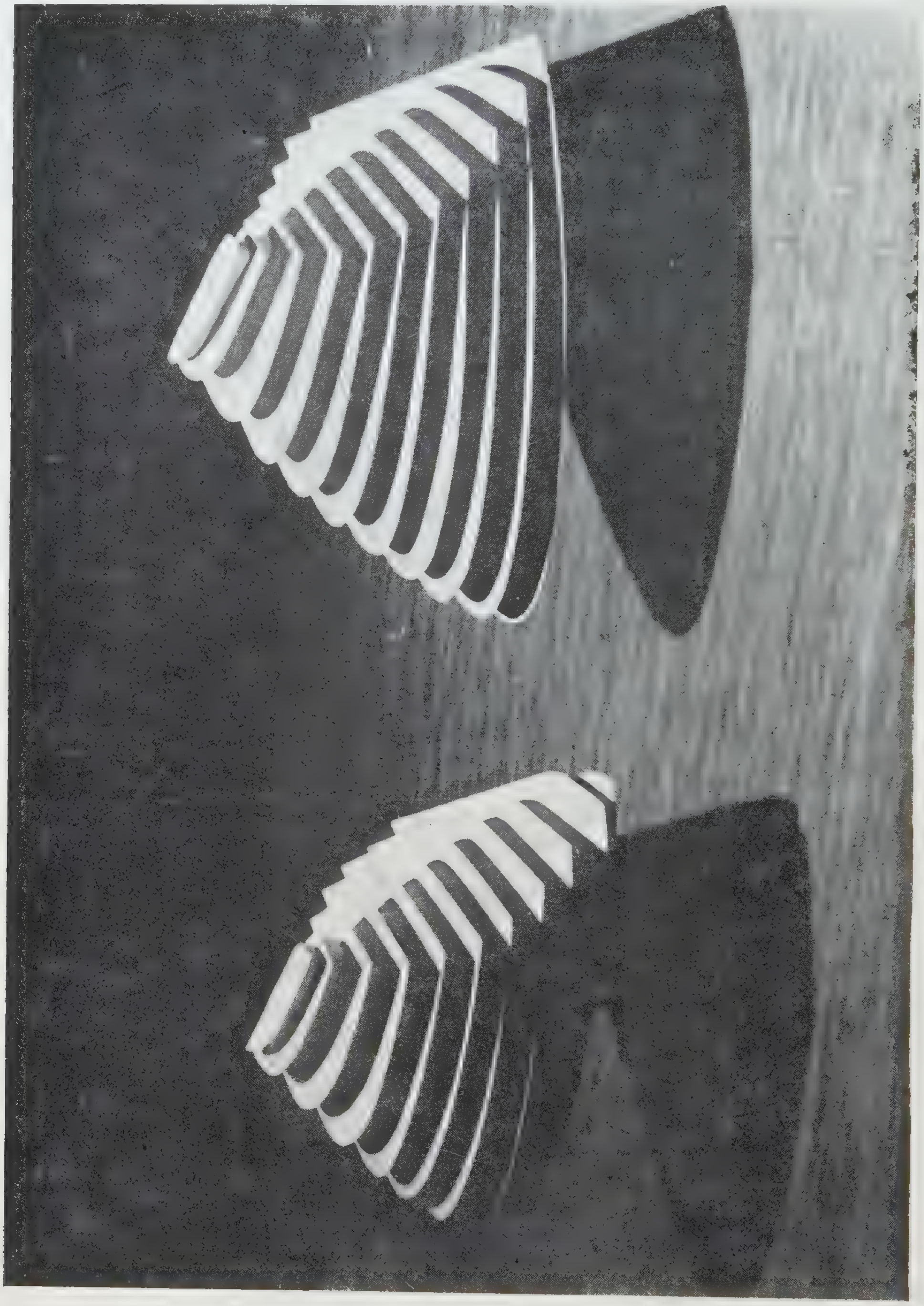
The complexity of the ultra-violet band system appearing in the spectrum of magnesium burning in air will be apparent from the reproduction given in the plate (*b*). Much of the presumably vibrational structure appears to be incompletely resolved even at a dispersion of 3·6 A./mm., as on our second-order

Table 2. Ultra-violet bands in the spectrum of magnesium burning in air

λ (I.A.)			Int.	ν vac.	λ (I.A.)			Int.	ν vac.
3594·23	V		0	27814·5	3772·8	R	A	3	26498
99·4	V		0	774·5	73·05	V	A	3	496·2
3612·1	? V		0	677	77·37	R		2	466·0
21·25	V		1	607	77·83	R		2	462·7
26·80	V		1	564·7	82·25	R	A	2	431·8
28·4	V		1	552·5	83·33	V		2	424·3
33·86	V	A	1	511·1	83·95	R		2	419·9
39·7	V		1	467	84·48	V		2	416·3
60·12	R		2	313·8	90·65	R	A	2	373·2
62·5	R		1	296	92·58	V	A	2	359·8
64·5	R		1	281	98·29	R		4	320·2
65·1	V		1	277	3802·6	V	A	2	290
71·9	R		1	226	04·23	R		3	279·1
72·5	V		1	222	05·28	R	A	5	271·8
74·73	R		2	205·2	10·28	R	A	5	237·4
84·0	R	A	2	137	15·60	R	A	5	200·8
84·92	V	A	2	129·9	16·5	R	A	5	195
89·07	V	A	2	099·4	23·8	R	A	5	145
90·61	R		2	088·1	24·21	V	A	5	141·8
98·64	V		2	029·3	35·74	V		5	063·2
3700·8	R		2	014	42·30	V		6	018·7
02·6	R		2	000	45·12	V		7	25999·6
03·78	M	A	3	26991·8	48·48	V	A	8	976·9
09·30	V	A	3	951·6	49·77	V	A	8	968·2
14·6	V		5	913	52·46	V	A	4	950·1
20·71	V	A	10	869·0	53·49	V	A	5	943·2
21·04	V	A	9	866·6	54·98	V	A	5	933·2
21·36	V	A	10	864·3	56·32	V	A	6	924·1
21·83	M	A	6	860·9	59·17	V		4	905·0
24·82	V	A	9	839·3	60·1	V	A	4	899
25·86	V	A	8	831·8	61·68	V		4	888·2
26·03	V	A	6	830·6	65·02	V		4	865·8
31·4	? V	A	7	792	65·49	V		4	862·6
31·92	V	A	7	788·3	76·88	V		1	786·7
32·26	V	A	3	785·8	80·18	V		1	764·7
40·65	V		2	725·7	82·43	V		3	749·8
41·42	R		2	720·3	3906·5	R		1	591
50·61	R	A	3	654·8	13·0	R		2	549
55·6	R	A	1	619	21·25	V		1	494·9
59·42	V	A	2	592·3	27·6	R		2	454
66·00	R	A	3	545·9	36·17	M		2	398·5
66·4	? V	A	3	543	46·0	V		2	335
69·7	? R	A	2	520	52·2	V		1	295
69·98	V	A	2	517·8	63·1	V		1	226
71·79	R		2	505·1	71·4	V		1	173
72·39	R		3	500·9	94·5	? V		0	027

The letters R, V indicate band degraded to red or violet: M indicates a maximum, and A denotes a band observed also in absorption.


λ
48
49
50
51
52
MgH
Mg
210
206
204
198
194
192
ν
(a)
λ
36
37
38
39
40
Mg
Mn
270
260
250
ν
(b)



a. McAdam colour solid.

b. Modified colour solid.

Figure 2 (*a* and *b*).

plates. The bands seem to form very closely spaced sequences, initially degraded to shorter wave-lengths, but the presence of bands degraded in the opposite direction suggests that the sequence difference may change sign at high v', v'' values. All attempts at a vibrational analysis have failed, and we conclude that work with higher dispersion is necessary.

The identity of the carrier must remain in doubt until such work has been done, but we would point out that the system is of considerable interest, particularly in view of the fact that we have observed it in absorption in the flames of certain pyrotechnic compositions containing magnesium.

The only reliable measurements of the main features of the system are those of Eder (1904), but his data apparently refer to maxima rather than to probable heads of bands. We therefore list wave-lengths and rough intensity figures of the more prominent heads in table 2.

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THE BRIGHTNESS OF PRESENT-DAY DYES

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Lecture given to the Colour Group 22 January 1944

§1. INTRODUCTION

In dye research laboratories, new dyes are continually being evolved, some of which ultimately become commercial products. Those which are so developed must clearly display advantages over the dyes already on the market, since the dye user would not otherwise change over from established products. The advantages shown by a new dye may be of many types, such as greater resistance to light or washing or easier application than existing dyes, but the aspect of greatest interest to the Colour Group is that of the colour of the dye. A new dye may be marketed solely because of its novel colour or outstanding brilliance, and it is obviously of great practical interest to the dye manufacturer to know just how the colour qualities of a dye may be improved and, in particular, the extent to which improvement in any given direction is possible, so that research may be directed towards the most promising field.

Improvement in the colour qualities of a dye may be obtained in two directions, namely, novelty of hue and increased "brightness". It is desirable that at the outset of the present paper the significance of the word *brightness* should be

defined. The dyer uses the word in its everyday sense, as when one refers to a "bright red coat", or a "bright green hat", and it is with this meaning that it will be employed here. The physicist, unfortunately, uses the same word in a quantitative manner, referring to the amount of light reflected from a surface. In order to avoid confusion it is proposed to use the term *lightness* to cover this latter usage. The *brightness* of the dyer covers a combination of *lightness* and *purity*. Thus if a comparison is being made of two samples of equal hue and equal purity, then the lighter will be termed the brighter, while if the patterns are of equal lightness but different purity, then the purer pattern will be termed the brighter. This matter has been discussed in some detail in an earlier paper (White, Vickerstaff and Waters, 1943).

Returning to the question of possible colour improvement, the main objective of the dye manufacturer is the production of greater brightness than is shown by existing dyes, the reason being that bright dyes can always be made duller if necessary whereas dull dyes cannot be brightened. There is not so much scope for the invention of dyes of novel hue, since there are already sufficient dyes to form a satisfactory colour circle, and intermediate hues can be obtained by mixture. In certain cases there may be advantages in having a homogeneous dye of a particular shade since it may be brighter than a mixture, and in any case a single dye is usually more easy to apply to material. There is some gap, for instance, in the yellow-green region of the hue circle.

Nevertheless, the predominant importance of brightness is fully realized in the colour-using trade, and dye manufacturers are constantly striving to produce brighter reds, brighter greens, brighter blues and brighter yellows than those already in existence. It is obvious that this process cannot be continued indefinitely. There must be a limit to the brightness which it is possible to attain in any particular hue. It may be that some existing dyes already approach that limit closely, so that attempts to improve them would be useless, while there may be other regions in which attempts to improve brightness would have much greater scope. It is clearly not possible to decide these matters by a mere inspection of the available colours, as there can be no innate knowledge of the attainable limit. However, the limits of purity and lightness which may be attained by surface colours have been defined by McAdam (1935), and it would seem a simple matter to compare real dyes with these limits and thus determine the hues offering most scope for improvement. It was with this object in mind that the present work was undertaken. The comparison was found to be a more difficult matter than appeared at first sight and although a fairly satisfactory basis of comparison was finally worked out, it is felt that the difficulties encountered are in many ways as interesting as the final conclusions, and it is therefore proposed to give a brief chronological account of the approach to this problem.

§ 2. BASIC IDEAS

As an introduction to the subject, the reasons for the existence of limits to the purity and lightness attainable may be briefly outlined. Any coloured surface can be defined in terms of the trichromatic or the monochromatic system, and such a definition is complete. The three variables involved are usually regarded as being completely independent, it being possible to vary any one whilst the

others remain constant. While this is true when applied to coloured light, it is not entirely true of surface colours such as painted panels or dyed fabrics. In such coloured surfaces, the effect of colour is produced by the absorption of part of the incident light, and all such surfaces must therefore have a lightness of less than 100%, since they are measured by comparison with a standard white surface which reflects all the incident light. Furthermore, it is clear that as more dye

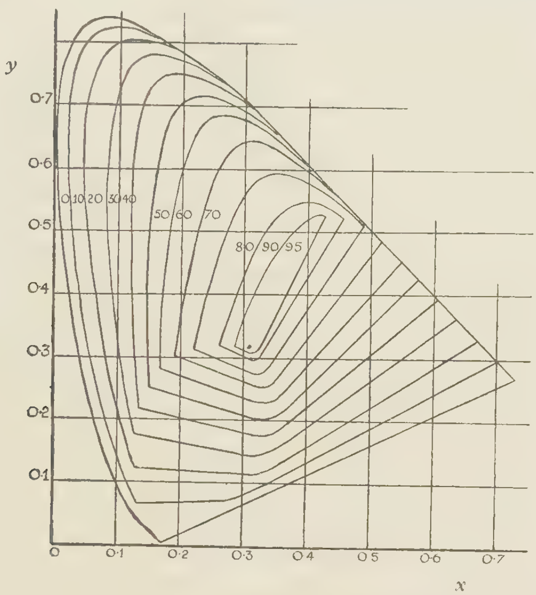

Figure 1 *a*.

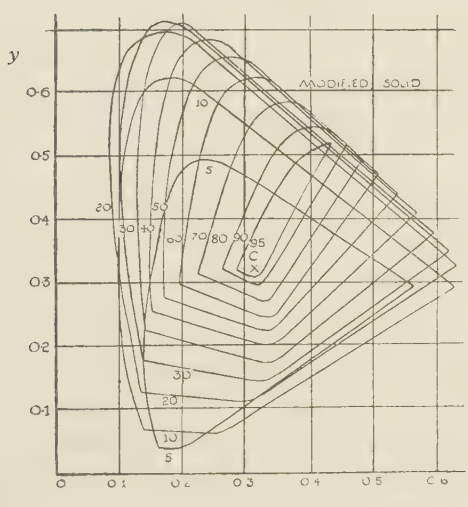

Figure 1 *b*.

applied to a surface, which thus differs more and more from white, so does the colour of the surface become purer, but at the same time darker. High purity and high lightness are thus mutually exclusive in the case of surface colours, and to this extent these two properties are not independent variables.

This question has been investigated in detail by McAdam, who has calculated In order to do this, McAdam first proved that the coloured surface will have maximum purity and lightness if the spectral reflection curve of the surface satisfies the following two conditions:

(1) The reflection factor at any wave-length must be either unity or zero.

(2) There must not be more than two transitions in the value of the reflection factor over the visible spectrum.

The application of these conditions leads to the conclusion that coloured surfaces possessing maximum purity and lightness must have rectangular-shaped spectral-reflection curves having not more than two absorption bands in the visible region. Curves of this type may be converted by normal methods into the corresponding trichromatic or monochromatic specifications, and thus it is possible to calculate the maximum possible lightness which a coloured surface can exhibit at any given hue and purity. The most convenient representation

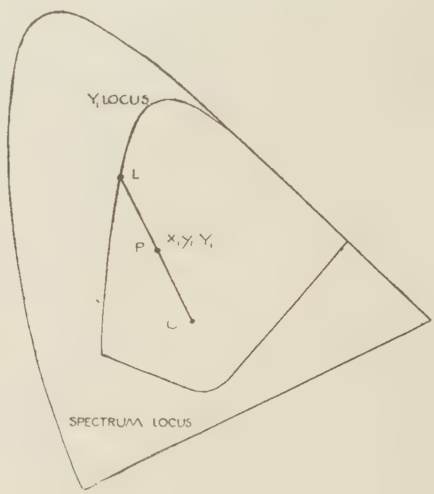

Figure 3.

of all the results is in the form of a colour solid within which all real coloured surfaces must lie. A contour map (after McAdam) of this colour solid is given in figure 1 *a* and a photograph in figure 2 *a*. The base of the solid is the x, y plane and the vertical ordinate is the lightness.

The limits of this colour solid provide the yardstick against which the achievements of real dyes must be measured. The difficulty which immediately arises is the exact manner in which the measurement is to be made. In a first attempt to overcome this difficulty, it was proposed to express the approach of a real dye to the ideal limits (its "efficiency") merely as the ratio of the excitation purity of the real sample to the excitation purity of the limit of the colour solid at the same hue and lightness. The method is illustrated in figure 3. A certain pattern has co-ordinates x_1, y_1, and lightness Y_1, and is, therefore, located at the point P. A cross-section of the colour solid at the same lightness level Y_1 has the contour shown, and the point P really lies in the plane of this cross-section. If C

e maximum possible purity of a coloured surface of any given hue and lightness. presents the position of illuminant C and if the line CP cuts the limit contour L, then it was proposed to define the efficiency (E_e) of pattern P as

$$E_e = \frac{CP}{CL} \times 100 = \frac{e_P}{e_L} \times 100,$$

iere e_P and e_L are the excitation purities of points P and L respectively.

The efficiency of a single dyed pattern can be expressed in this way without ıch difficulty, but, unfortunately, the efficiency of a dye varies with the pth of shade employed. As the amount of dye on a pattern increases, so does purity up to a certain point. If more dye is placed on the pattern after this int has been reached then the purity usually decreases. The dyer expresses s by saying that the pattern becomes duller at high concentrations. The iciency of dyed patterns when each pattern is compared against its own limiting int usually behaves in a similar manner, rising to a peak and falling again. For s reason it was decided to define the excitation efficiency of a dye as the ximum efficiency which could be obtained on dyed fabric at any depth of shade, d in order to determine this it was necessary to measure a whole range of dyeings gradually increasing strengths for each dye. The dyeing having maximum iciency was then selected as representing the efficiency of the dye itself.

§ 3. EXPLORATORY EXAMINATION

As an example of the method and the type of variation encountered, the comte results for one dye, Victoria Pure Blue BOS, are given in table 1. In the

Table 1. Excitation efficiency of dyeings of Victoria Pure Blue BOS

% dye n wool	x	y	Actual lightness	Excitation purity	Dominant wave-length	Theoretical lightness	Excitation efficiency
			%		A.	%	%
0·06	189	194	16·7	58·0	4774	20·9	68
0·125	175	149	11·0	69·0	4733	13·8	78
0·25	165	113	6·6	78·5	4696	8·3	82
0·50	168	093	4·4	81·2	4655	5·5	85
1·00	172	088	3·3	81·0	4630	4·1	85
2·00	183	082	2·6	79·8	4570	3·3	85
3·00	190	092	2·1	76·0	4540	2·6	79
4·00	201	099	2·0	72·0	4480	2·5	75

column of the table is the percentage of dye applied to the cloth, and in the t three columns the trichromatic co-ordinates and the lightness of the resulting ngs in Illuminant C as measured on the Donaldson colorimeter. Then ws the dominant wave-length and excitation purity obtained by plotting the rdinates on the graphs given in Hardy's *Handbook of Colorimetry*, with Illuant C as white light. The penultimate column gives the approximate lightwhich the patterns would have if the substrate were perfectly reflecting. yed woollen cloth of the type used in these investigations is slightly yellowish has a lightness of 80% (mean of several measurements). Since McAdam's

data are calculated on the assumption that the reflectance of an uncoloured surface is 100%, it is necessary in assessing the efficiency of a dye to make some correction for the absorption of the substrate; by dividing the actual lightness values by 0·8 an approximate value is obtained for the lightness of a dyeing on a perfect substrate. The error introduced by the fact that the undyed wool is not unselective in absorption is very small. Finally, the efficiency of each pattern is shown, from which it is clear that the maximum excitation efficiency attained by this particular dye is 85%.

The method was empirical, but it did provide a first basis for a comparison between dyes of different hues. Working on this basis, a number of dyes were examined. The dyes were of various types and included acid dyes on wool, vat dyes on cotton and pigments in oil painted on glass. Efficiencies varying from 40% to over 90% were obtained, and it was found that there was a general consistency in the results on the different types of dye, greens having low efficiency, and yellows high efficiency. The variation of efficiency with colour is shown in

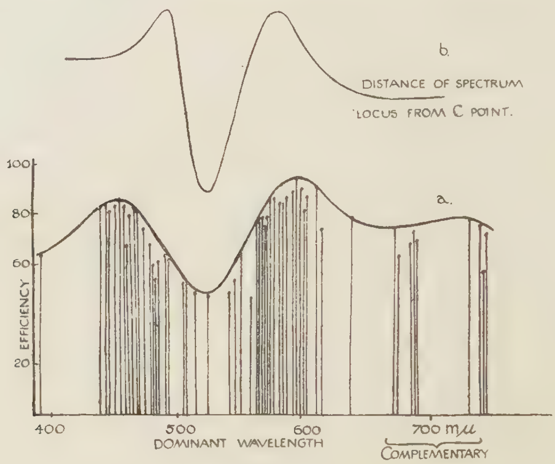

Figure 4 (*a* and *b*).

figure 4, in which the efficiency of 61 dyes or pigments is plotted against the dominant wave-length of the respective colours. All the colours tested have efficiencies falling within the area bounded by the smooth continuous curve, which has two particularly characteristic regions, namely that of very high efficiency near 600 mμ (yellows and oranges) and that of low efficiency near 520 mμ (greens). Examination of this diagram indicates that the points of maximum and minimum efficiency are located at wave-lengths corresponding to the points at which the spectrum locus is respectively nearest to and furthest from the point representing Illuminant C. This immediately suggests that efficiency is in some way determined by the geometry of the chromaticity diagram. and in fact the effect may be traced to the use of excitation purity, or distance in measuring efficiency. Excitation purity was chosen for this purpose because it is easier to determine than colorimetric purity, and it was thought that a comparison of the excitation purity of a real surface with the theoretical maximum excitation purity at the same lightness would be a sufficient measure of efficiency, and would indicate

the limits which can theoretically be obtained, just as well as the more complex colorimetric efficiency. Further consideration shows, however, that although the limits are indicated in this way, the scale of efficiency is not uniform over the spectrum, so that comparison of dyes of differing hue is not justified.

The concept of efficiency would appear to be placed upon a sounder basis if colorimetric purity is employed, as this takes due regard of the fact that the relative " brightness " of the spectrum varies with wave-length.

§ 4. REVISED FORMULATION

Accordingly, the previous results were recalculated to give the colorimetric efficiency E_c according to the definition

$$E_c = \frac{C_P}{C_L} \times 100,$$

where C_P and C_L are the colorimetric purities of P and L respectively. On this basis, there seems some justification for assuming that the results will be independent of hue.

The colorimetric efficiencies are plotted against dominant wave-length in figure 5 *a*, from which it will be seen that the efficiency now attains a maximum

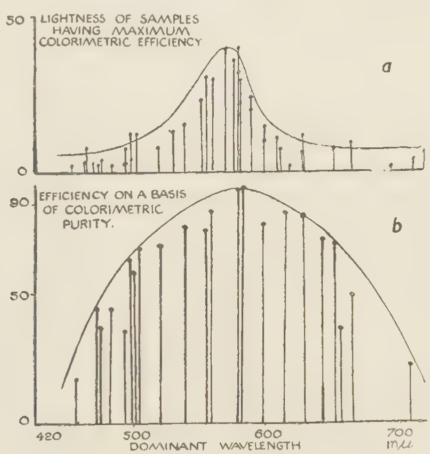

Figure 5 (*a* and *b*).

value in the green and falls away steadily on either side. After some consideration it was found that if the lightness of the patterns giving maximum purity is plotted against dominant wave length (figure 5 *b*) the curve shows a maximum in the same position as the efficiency curve. Thus the efficiency must be related in some way to the lightness of the patterns. This behaviour was finally attributed to the light scattered from the front surface of the patterns. When light falls on any surface, a portion is reflected without penetrating the material, and, therefore, consists of unchanged white light. The remainder of the light passes into the material, suffers partial absorption and emerges as coloured light. The fraction of light reflected from the front surface is practically independent of the colour of the dye, and on the average has a value of about 2% of the incident light for most textile materials, although it is modified by many factors, such as

the surface structure of the dyed material and the refractive index of the medium. If the efficiency of a pattern is measured at a relatively high lightness, then the addition of 2% white light will have little effect upon the colorimetric purity of the pattern, but if it is measured at a lightness of, say, only 5%, then the white surface light will comprise 40% of all the light coming from the pattern and will reduce the colorimetric purity very greatly, so that the efficiency will also decrease. The variation of colorimetric efficiency with wave-length shown in figure 5 is due, therefore, to the presence of this surface light, and an attempt was made to correct for this effect.

One of the conditions laid down by McAdam in his derivation of the colour solid which is the basis of the present discussion was that the reflection factor at any wave-length must be either zero or unity. With any real coloured surface this condition cannot be attained, for even if a dyed material did absorb completely all the light at some wave-lengths, its over-all reflection factor would still be 2% owing to the surface scattering. In order to correct for this, a new colour solid was constructed on the assumption that the reflection factor at all wave-lengths, for patterns having maximum purity and lightness, is either 1 or 0·02.

Table 2. Trichromatic co-ordinates of contours of maximum purity at constant lightness for surfaces reflecting a minimum of 2% of the incident light

5% lightness		10% lightness		20% lightness		30% lightness		40% lightness	
x	y	x	y	x	y	x	y	x	y
0·570	0·292	0·634	0·294	0·634	0·325	0·623	0·348	0·600	0·376
440	378	500	405	500	445	500	461	400	562
340	447	400	483	400	536	400	552	300	642
260	496	300	561	300	621	300	637	240	686
240	502	200	614	240	667	240	681	220	700
220	502	200	621	200	690	200	704	200	707
200	489	180	624	180	698	180	710	180	702
180	452	160	622	160	699	160	709	160	678
165	400	140	609	140	692	140	698	138	600
148	300	125	580	120	679	111	600	128	500
138	200	108	500	100	642	104	500	128	400
140	150	100	400	091	600	106	400	132	300
145	100	100	350	086	500	118	300	138	220
159	040	101	300	092	400	134	176	160	215
180	040	108	200	104	300	160	172	200	204
200	042	117	140	120	200	200	164	280	183
210	044	127	100	134	126	260	154	320	173
220	050	139	068	160	124	300	146	330	172
260	076	160	066	200	120	320	144	340	174
400	175	180	064	240	116	340	149	360	184
		200	060	280	112	360	160	400	214
		240	059	300	113	500	260	500	296
		260	064	320	120				
		280	074	360	143				
		300	087	500	236				
		450	180						

Table 2 (*continued*)

50% lightness		60% lightness		70% lightness		80% lightness		90% lightness		95% lightness	
x	*y*	*x*	*y*	*x*	*y*	*x*	*y*	*x*	*y*	*x*	*y*
0·571	0·408	0·538	0·442	0·510	0·470	0·483	0·496	0·455	0·523	0·430	0·520
400	572	400	573	400	574	400	574	420	596	400	508
320	639	320	638	360	606	380	584	400	547	360	470
300	654	300	649	340	617	360	588	380	540	320	400
260	680	280	660	320	625	340	582	340	500	288	320
240	688	260	660	300	625	314	560	292	400	308	308
220	687	240	652	280	616	279	500	264	318	314	307
200	672	211	600	265	600	246	400	300	301	320	309
172	600	187	500	225	500	224	312	320	296	328	320
156	500	175	400	207	400	252	300	330	304	369	400
150	400	172	300	196	300	320	271	400	422		
150	300	172	280	240	280	340	277				
150	253	200	268	320	248	400	368				
200	237	300	232	330	246						
300	208	320	226	340	248						
320	202	330	224	360	270						
330	201	340	225	440	377						
340	203	360	240								
360	212	460	353								
400	248										
500	341										

The actual value of the first surface reflection will differ according to whether wool, cotton or glass plates are examined, but in order to avoid the labour of computing a fresh solid for each surface, a value of 2% for the scattered light was assumed throughout. This is probably near enough to the real value in the case of textile fabrics, since the lightness of black dyeings rarely falls below this figure. In the case of glass plates coated with pigments the value is probably a little high.

The new solid was constructed by the method described by McAdam, using tables of running sums for the separate trichromatic functions constructed from the tables in Hardy's *Handbook of Colorimetry*. The resulting colour solid is shown in figures 1 *b* and 2 *b* for comparison with the unmodified solid, and the marked reduction in the possibilities of high excitation purity in the greens may be noted. The co-ordinates of several points on the loci at various lightness levels are given in table 2.

The efficiency of the patterns was now redetermined on the basis of this new colour solid, again comparing the colorimetric purity of each pattern with that of the theoretical limits at the same lightness. When this comparison was carried out at different dye concentrations, it was found that the efficiency of each dye increased steadily with increasing concentration and showed no maximum. This might indeed have been anticipated from the behaviour of dye solutions. If the concentration of dye in a solution is increased, the purity of the transmitted light increases continuously and ultimately reaches 100% if the dye is sufficiently

soluble. This is because all dyes must have a maximum transmission of light somewhere in the spectrum, and, at a sufficient concentration, the light transmitted will therefore tend to become monochromatic. In the case of dyed patterns, however, the behaviour is different, the purity increasing to a maximum value as the concentration increases, and then decreasing; this effect is due to the uncoloured surface-scattered light. Consequently, if a correction is applied for this factor, then the efficiency of dyed patterns must also approach 100% at very high concentrations.

Clearly, then, while the concept of colorimetric efficiency can be applied to any particular pattern or surface, it cannot be used to attach any value to a specific dye, since it varies with concentration. It is possible to overcome this difficulty by specifying that the efficiency must be measured at some particular lightness or purity, or even dye concentration, but such methods are purely arbitrary, and would give unequal weight to colours of different hue. It may also be mentioned that the alternative method of measuring efficiency, as the percentage of the limiting lightness which a pattern attains at the same hue and purity, is open to similar objections, namely, that efficiency varies with concentration, and that to select an arbitrary purity at which efficiency should be measured would be to discriminate against certain hues. Many other possibilities were considered, but all suffered from one or more of the defects of arbitrariness, non-uniformity of scale, or variation in value with concentration. Another method which was investigated, in a tentative manner, was to compare the shape of the absorption curves obtained by plotting optical density of a solution against wave-length with the corresponding rectangular curves postulated by McAdam. The advantage of this approach is that the shape of the curve is independent of concentration; but there are many drawbacks, such as the fact that efficiency measured in this way is a purely empirical function which has no bearing on the visual effect, and that, with the apparatus available, practical measurements were limited to solutions, whereas interest chiefly lies with dyed materials, and in many cases the colour of a dye on the fibre may be different from its colour in solution.

§ 5. FINAL METHOD

At this stage the problem was reviewed in an attempt to define more clearly the aim of the investigation. There seemed to be several objectives possible, but after careful consideration it was decided to concentrate attention on trying to find a means for measuring the possibilities of improvement in the colour of a dye in terms of sensation steps rather than in physical units. The reason for this is purely practical, for the dye-maker is interested only in the visual sensation produced by a certain improvement in colour, and not in its physical dimensions. The most satisfactory approach appeared to consist in a determination of the number of perceptible steps of change by which a given colour differs from the ideal McAdam limits. It might appear at first sight that this could be ascertained in a fairly satisfactory manner by plotting the points upon a uniform chromaticity diagram of the type suggested by Judd (1935) or by Breckenridge and Schraub (1939). Unfortunately, such diagrams are designed to apply only to lights of nearly equal intensity, and cannot be applied to questions involving surface colours, which necessarily vary very considerably in lightness. The

only satisfactory solution is to measure the distance between the real dye and the ideal limit inside a uniform chromaticity colour solid, in which, by definition, unit distance in any direction corresponds to an equal difference in colour sensation, and which is based upon the known behaviour of surface colours.

The only available information on a colour solid of this type is upon the Munsell colour system, the patterns of which have been specified in terms of trichromatic units in recent publications (Kelly, Gibson and Nickerson, 1943).

In the Munsell system, the colour attributes of a pattern are expressed in terms of the three quantities *hue*, *chroma* and *value*. These correspond qualitatively to the *hue*, *purity* and *lightness*, respectively, of the monochromatic system, but quantitatively the relationship is complex and cannot be mathematically defined, since the monochromatic system is an expression of colour in terms of physical quantities, whereas the Munsell system represents an attempt to arrange colours in such a manner that the visual spacing appears uniform and regular. In view of the recent extensive smoothing of the spacing of the Munsell colours, based on visual assessments (Newhall, Nickerson and Judd,

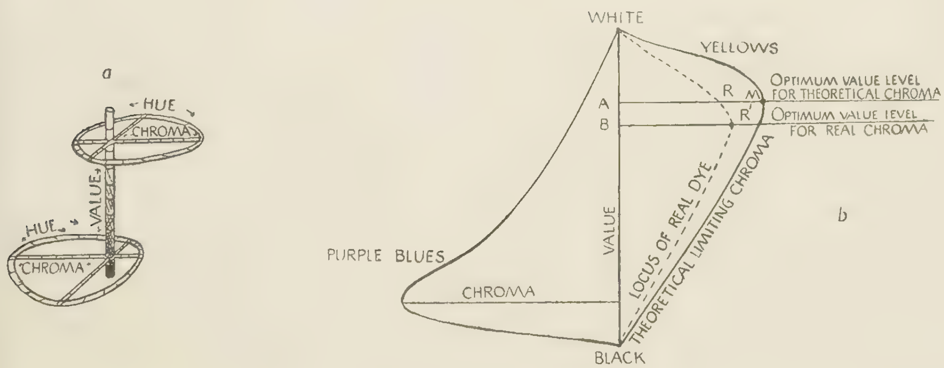

Figure 6 (*a* and *b*).

1943), there is a reasonable prospect that a unit difference of chroma at any value (lightness), and in any hue, will produce a similar visual or mental effect. This system thus appears to offer the greatest promise of providing a method whereby the visual possibilities of colour improvement can be assessed in a way which will be independent of the hue and lightness of the patterns examined, as far as uniformity of scale is concerned.

The possibilities of improvement, however, will still remain to some extent dependent upon lightness. The reason for this can best be appreciated by considering the shape of the Munsell colour solid (figure 6 *a*). In this, the achromatic series of greys between black and white form the axis from which the various hues radiate in increasing chroma. If a cross-section of this colour solid be taken by passing a plane through the achromatic axis, a typical section will be as shown in figure 6 *b*, which represents a cross-section through the yellow and the complementary purple-blue hues. The outer limits of this cross-section represent the colours of McAdam's limiting colour solid, after correction for surface-scattered light. It will be seen that in both halves of the section shown, the chroma first increases as the value decreases from white, but then reaches a maximum and

decreases again as the value approaches zero, or black. In other words, there can be no colour in either black or white, but only at intermediate values. It is important to note that different hues attain their maximum chroma at different values. Thus yellows can reach high chroma or colourfulness with small light absorption, but high chroma in purples can only be reached at low values, a phenomenon which is due to the variable sensitivity of the eye to the different colours of the spectrum.

In figure 6 the points representing dyeings of a typical real dye in gradually increasing strengths have also been plotted, and it will be seen that the maximum chroma attainable by a real dye is less than that of the limiting locus and, furthermore, is attained at a lower level of value. It is also clear that the number of chroma steps separating the real dye from the theoretical limit varies with the value level at which the comparison is made, so that the problem still remains of selecting for the comparison a value level which will be equally satisfactory for all hues. The best solution of this problem seems to lie in a comparison at the value level at which the ideal locus attains maximum chroma (A in figure 6), since as the real dye becomes more perfect so does its locus approach the limiting locus. The value level in question will of course differ for each hue.

It is perhaps desirable to digress a little here in order to consider a point raised by Mr. R. G. Horner in the discussion after the lecture. He suggested that in trying to define the efficiency of a dye in terms of a single number, we may be attempting the impossible. It may be that inefficiency can only be adequately described by a statement of both the chroma and value deficiencies of the real dye. This may well be the case, but it is felt that, from the dye manufacturer's point of view, a single number is always preferable to a more complex description, as it leads to no ambiguity as to which of two dyes is the better. Therefore, unless it can be shown conclusively that a single function is inadequate to describe the defects of dyes, there seems no reason to increase the complexity. Furthermore, by comparing the theoretical maximum chroma with the chroma of the real dye at the same level of value, instead of comparing the maximum chroma attainable by the real dye with the theoretical maximum, we are in effect introducing an empirical correction for the fact that the real maximum chroma is attained at a lower value level. Examination of figure 6 *b* will make this point clearer, for it is proposed to measure the chroma deficiency indicated by the distance RM, rather than the difference between the maximum chromas (AM − BR′). From a rather superficial examination of the results obtained and comparison with visual observations on the brightness of the dyes examined, the proposed measurement appears to be fairly satisfactory, but it may well be found, on a more detailed scrutiny, that anomalies appear.

After due consideration it was decided to adopt the above proposal for the determination of inefficiency. Before this can be put into practice, however, it is necessary to know the actual shape of the Munsell colour solid, in order that the optimum value level may be selected for the comparison of a dye of any specific hue. The method of determining this shape was as follows. The trichromatic coefficients of all the Munsell colours of value 6 (for example) were plotted on a chromaticity diagram and isochroma lines were drawn through the points of equal chroma. The figures for the co-ordinates of the Munsell colours

were taken from the recent publication of the Optical Society of America, in which the spacings have been smoothed and extrapolated to the theoretical limits. On this diagram was superimposed the theoretical limit contour corrected for surface-scattered white light for colours of that particular lightness (30%) or Munsell value (Newhall *et al.*, 1943). The resulting diagram is shown in figure 8. Similar diagrams were prepared for value levels of 3, 4, 5, 7 and 9. Value levels below 3 were not studied, for a Munsell value of 2 corresponds to a lightness of only 3·4%, and since the patterns have a matt surface, at least 50% of the light reflected from them must consist of surface-scattered white light. The accuracy with which the theoretical limits may be defined is thus very low. In the present writer's opinion, Munsell patterns of value 1 (1·2% lightness) are unrealizable in practice, and the extrapolation of the chroma of patterns of this value to the spectrum locus is meaningless.

The resulting set of six diagrams of the type shown in figure 8 represents cross-sections of the Munsell colour solid. Cross-sections at right angles to these were then prepared by passing planes through the black-white axis at various

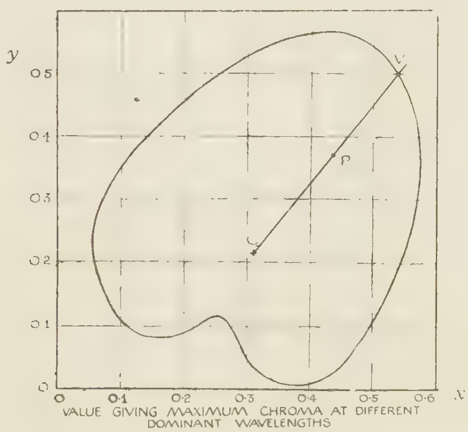

Figure 7.

hues and determining the limiting chroma at each value level. By plotting chroma against value, curves of the type of figure 6 were obtained, from which the value level yielding maximum chroma in that particular hue plane could be determined. Such cross-sections were cut at 26 different hues spaced fairly evenly round the colour circle, with a rather greater concentration around the ends of the spectrum locus, where abrupt changes may occur. The value levels yielding maximum chroma and the corresponding chroma are shown in table 3 but in practical use it is more convenient to express the results in graphical form, shown in figure 7. This diagram is constructed on the standard chromaticity diagram, and is so contrived that if a straight line is drawn through C to cut the heart-shaped locus at V, the distance CV indicates the value at which the ideal dye having the hue of points on CV attains maximum chroma.

The whole procedure involved in determining the inefficiency of any real dye will now be reviewed briefly, in order to clarify the position and indicate the practical steps which are involved. A dyeing is first prepared and measured in

the Donaldson colorimeter or in any other suitable instrument. The trichromatic co-ordinates are plotted in figure 7 at P and the line CP drawn to cut the locus at V. The distance CV is measured in units of value (1 unit of value = 0·04 units of x), and this indicates the value at which the ideal colour of the same hue at P attains its maximum chroma. If the value of the actual pattern does not coincide with the value so determined, it must be varied by increasing or decreasing the amount of dye applied to the cloth until it is of the correct value. Fortunately,

Table 3. Value levels yielding maximum chroma on cross-section through modified colour solid

Cross-section through C point and point in column below		Value level yielding maximum chroma	Maximum chroma
x	y		
0·310	0·700	7·7	20·5
0·400	0·700	9·1	18·0
0·500	0·700	9·5	17·0
0·600	0·700	9·1	17·0
0·700	0·594	7·8	16·5
0·700	0·480	7·0	17·0
0·700	0·400	6·3	18·5
0·700	0·360	6·0	19·0
0·700	0·316	5·6	19·5
0·700	0·200	5·4	20·5
0·600	0·104	5·4	22·0
0·500	0·000	5·4	26·0
0·366	0·000	5·0	30·0
0·310	0·000	4·5	32·0
0·198	0·000	3·0	[35·0]
0·122	0·000	3·0	[30·0]
0·000	0·000	4·8	19·0
0·000	0·145	5·8	16·0
0·000	0·226	6·0	17·0
0·000	0·316	6·1	19·5
0·000	0·400	6·1	21·5
0·000	0·500	6·2	24·0
0·000	0·600	6·2	25·0
0·000	0·800	6·5	26·5
0·100	0·800	6·6	27·0
0·200	0·900	7·2	24·5

the hue does not usually change greatly with depth of shade, for if it did, it would be necessary to proceed by successive approximation, redetermining the optimum value level for each new pattern until coincidence was obtained. A pattern of the correct value having been obtained, its trichromatic co-ordinates are determined and plotted on a cross-section of the colour solid at the same value. This cross-section is mapped out with the appropriate isochroma contours as shown in the example in figure 8, and by drawing a line from C through P to cut the limiting locus at L, the number of steps of chroma improvement possible is immediately evident.

Proceeding in this way, the inefficiency of a number of dyes has been determined. The results are given in detail in table 4, which shows the percentage depth of shade needed to produce the required value for the particular hue of each dye, the trichromatic co-ordinates of the corresponding pattern and the actual lightness (corrected for the absorption of the substrate), the dominant wavelength, value, chroma, limiting chroma, and chroma improvement possible. The dyes are arranged in the table in order of hue. It should be noted that the dyeings here presented are not necessarily of the same depth of shade as those used in the earlier investigations on colorimetric and excitation efficiency.

From the rather limited number of results available, it appears that reds and yellows are highly efficient, blue-greens and bluish-reds less so, and purples and greens very inefficient. It seems unlikely that this variation can again be explained by any systematic error in the method of expression. Examination of typical absorption curves for the six primary colours (additive and subtractive)

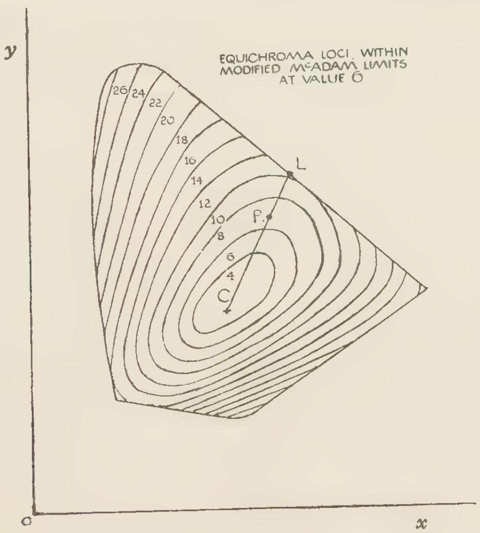

Figure 8.

shows that only in green and purple are there two absorption band edges which are both in the visible spectrum. For the production of the other four colours it is necessary only to have one band edge lying in the visible region. Since it is the sloping character of this band edge as compared with the vertical band edge of the ideal colours which produces inefficiency, it is obvious that greens and purples are almost certain to be the least efficient of colours, and this is confirmed by the present measurements. There is no obvious reason why blue-green dyes should be less efficient than yellows, but in actual fact they are less efficient, and this is probably due to the presence in all the dyes examined of a small secondary absorption in the far blue.

The case of Rhodamine BS is exceptional and interesting. It has a very high efficiency by any criteria, and, indeed, at certain lightnesses its excitation or colorimetric efficiency exceeds 100%. In other words, the points representing the pattern lie outside the colour solid. This result was regarded with some

Table 4. Chroma attained by dyes at value level giving theoretical optimum chroma

Dye	Dominant wave-length (A.)	Value level for maximum possible chroma	Light-ness	% depth of shade	x	y	Chroma	Limiting chroma	Improve-ment possible
Coomassie Violet RS	4540	3·0	6·6	0·8	0·192	0·096	18·5	30·5	12·0
Victoria Pure Blue BOS	4680	3·0	6·6	0·4	0·165	0·102	16·0	22·0	6·0
Coomassie Brilliant Blue FFS	4710	3·5	9·0	1·5	0·176	0·136	13·5	21·0	7·5
Alizarine Supra Sky R	4730	3·7	10·1	1·3	0·178	0·150	13·0	19·0	6·0
Disulphine Blue FFS	4830	5·5	24·6	1·0	0·194	0·243	9·5	15·5	6·0
Disulphine Green BS	4928	6·3	33·7	0·25	0·188	0·335	12·5	22·0	9·5
Carbolan Green GS	4950	6·3	33·7	0·20	0·258	0·334	5·0	23·0	18·0
Lissamine Green VS	5010	6·4	34·9	0·6	0·216	0·392	12·0	24·0	12·0
Lissamine Green VS 25% } Quinoline Yellow AS 75% }	5365	6·9	41·6	0·8	0·265	0·511	14·0	25·0	11·0
Lissamine Green VS 2·5% } Quinoline Yellow AS 97·5% }	5578	7·2	46·0	4·0	0·339	0·554	13·5	16·0	2·5
Carbolan Yellow 3GS	5738	9·1	80·1	0·8	0·437	0·484	14·0	16·0	2·0
Quinoline Yellow AS	5768	9·0	78·7	0·4	0·448	0·462	12·0	17·0	5·0
Coomassie Yellow RS	5775	8·8	74·0	0·15	0·414	0·421	8·0	17·0	9·0
Naphthalene Orange ROS	5980	6·5	36·0	0·5	0·553	0·368	15·5	17·0	1·5
Naphthalene Scarlet RS	6100	6·0	30·1	0·8	0·530	0·327	15·5	20·0	4·5
Coosmasie Red PGS	6105	5·9	28·9	0·3	0·511	0·325	14·0	20·0	6·0
Naphthalene Red JS	6230	5·8	27·8	0·25	0·490	0·311	14·0	19·5	5·5
Naphthalene Scarlet 6RS	7000	5·8	27·8	0·5	0·503	0·294	16·0	19·5	3·5
Rhodamine BS	4956 c	5·4	23·6	4·0	0·493	0·245	19·5	19·5	0·0
Carbolan Crimson BS	4975 c	5·4	23·6	0·25	0·432	0·251	15·0	22·0	7·0
Coomassie Violet 2RS	5032 c	5·5	24·6	0·25	0·398	0·230	16·0	23·0	7·0
Lissamine Fast Red 7BPS	5075 c	5·6	25·6	0·20	0·370	0·240	13·0	24·0	11·0
Carbolan Violet 2RS	5640 c	3·2	7·5	0·8	0·264	0·172	10·5	35·0	14·5

suspicion at first, but repeated measurements have confirmed its truth. Consideration of the known fluorescent properties of this dye indicated that such a behaviour might result if the dye absorbs visible radiation and then re-emits part or all of this as visible radiation of longer wave-length. A simple experiment sufficed to show that this was the true explanation. The standard magnesium oxide screen, a piece of white wool and a piece of wool dyed with Rhodamine BS were placed in the Donaldson colorimeter, illuminated with white light, and measured with a Wratten trichromatic red filter interposed between the eye and the pattern. The relative lightness of the patterns measured in this way was: magnesium oxide 98%, white wool 75%, Rhodamine dyeing 117%. Thus the Rhodamine BS is absorbing green light and re-emitting it as red, and in consequence the patterns can lie outside the McAdam colour solid, which is based on the assumption that surface colour is produced by light absorption only.

§ 6. CONCLUSIONS

From the above results it is considered that the chroma deficiency of a dye at the optimum value level of the appropriate hue provides a satisfactory measurement of the efficiency of the dye and the possibilities of visual improvement in brightness which remain. The results obtained by this method, on a number of dyes of differing hues, seem to show that those colours which have only one absorption band edge in the visible spectrum are more efficient than those with two, as might be expected.

From a more practical aspect it is considered that this method of measurement provides a sound basis for the quantitative comparison of the brightness of dyes of all hues, although it will be most precise and possibly most useful when the dyes compared are of similar hue. The results have also shown that in certain colours commercial dyes leave little room for improvement.

§ 7. ACKNOWLEDGMENT

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RESONANCE IN PRECESSIONAL STATES OF DIATOMIC MOLECULES

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ABSTRACT. Examples of electronic states described by van Vleck as "pure precession" are found in the Hg, Cd and Zn halide spectra and also with InO and GaO. These are shown to be in close resonance and probably have abnormally large Λ-type doubling. An interpretation of the spectra of InO and GaO is given and a potential-energy diagram is presented for these molecules and also for TlO.

§ 1. INTRODUCTION

In van Vleck's theoretical treatment of Λ-type and spin doubling in electronic states of diatomic molecules, it is shown that simple relations can be derived for the doubling constants for Σ and Π states if they are related to one another in a manner described by him as "pure precession". Such states act as though they have identical electron configurations, except that one has $\Lambda=0$ in the Σ state and $\Lambda=1$ in the corresponding Π state, whilst each retains the same atomic L vector, which remains quantized in the molecule whilst precessing round the electric axis. If there is only one valence electron outside closed shells, then λ and l here replace Λ and L. In addition, even the principal quantum number n of an atom may retain its significance on entry into a molecule.

Mulliken and Christy extended this work and applied the results to a number of molecules for which doubling data were available, and were able to verify van Vleck's work with the following hydrides: BeH, MgH, CaH, ZnH, CdH, HgH, CH, SiH and OH, and also with the homonuclear molecules He_2, Li_2 and Na_2. With the hydrides the results were interpreted on the assumption that the molecule is similar to the united atom, with the electrons, except that of H, retaining their atomic quantum numbers. For example, it is known that the normal $^2\Sigma$ and excited $^2\Pi$ states are related to the separated atoms as follows:

$$\text{Hg, } 6s^2 \; {}^1S + \text{H}, 1s\,{}^2S \rightarrow \text{HgH}, {}^2\Sigma^+,$$
$$\text{Hg, } 6s6p \; {}^3P + \text{H}, 1s\,{}^2S \rightarrow \text{HgH}, {}^2\Pi.$$

If the H electron in the molecule were still essentially a $1s$ electron, it would be possible to write

$$\text{HgH} \quad 6s\sigma)^2\sigma 1s\,{}^2\Sigma \quad \text{and} \quad 6s\sigma 6p\pi)\sigma 1s\,{}^2\Pi.$$

The electron configuration of both states would be the same except for the replacement of the $6s\sigma$ by the $6p\pi$. Now these orbits differ in l and hence cannot be related precessionally, whereas evidence from the Λ-type doubling shows

that the spectrum derives from two states which are so related. Hence it must be supposed that the H $1s$ electron becomes a $6p\sigma$ in the molecule, thus giving $6s\sigma)^2 6p\sigma$, $^2\Sigma$ and $6s\sigma)^2 6p\pi$, $^2\Pi$ for the two states being similar to the $6s^2 6p$ configuration of the united atom Tl. This example illustrates the importance of the Λ-type doubling in deciding which of possible configurations is the correct one.

With He_2, Li_2 and Na_2 the results were similarly interpreted in terms of the quantum numbers of the separated atoms.

The magnitude of the Λ-type and spin doubling is dependent upon the separation of the Σ and Π states, $\nu_{\pi,\Sigma}$ being larger the smaller the separation, i.e. the closer the two precessional states the greater the resonance shown in the fine structure. The largest Λ-type doubling coefficient discussed by Mulliken is that of CaH, where $\nu_{\pi,\Sigma}$ is 1300 cm.$^{-1}$.

The objects of this paper are (*a*) to point out the existence of even closer resonance between precessional states in the Zn, Cd and Hg halides, and (*b*) to interpret the spectra of the oxides of In, Ga and Tl in terms of similar close resonating precessional states.

§ 2. RESONANCE IN Zn, Cd AND Hg HALIDES

In a recent paper the author showed that the u.v. system of bands for the molecule HgF were due to a $^2\Pi - {}^2\Sigma$ transition (Howell, 1943). It was also found that there existed a close relation between the splitting of the $^2\Pi$ state and the coupling factor a of the $6s6p\,{}^3P$ state of Hg, a relation which could only be interpreted as indicating that the Hg $6p$ electron retained its l value in the molecule, becoming a $p\pi$. Further, the close proximity of the system to the Hg ground line * $^3P_1 - {}^1S$ meant that the principal quantum number n was also retained in the molecule. In short, the transition was the molecular analogue of the atomic transition $6s$ to $6p$, and can be described as occurring between atomic orbitals $6s\sigma$ and $6p\pi$. The electron configurations were therefore represented as $\pi^4 6s\sigma 6p\pi\ {}^2\Pi - \pi^4\ 6s\sigma\ {}^2\Sigma$.

Probably a better representation would be $6s\sigma 6p\pi)\pi^4\sigma\ {}^2\Pi \leftarrow 6s\sigma)^2\pi^4\,\sigma\,{}^2\Sigma$, which implies that the Hg atom largely retains its quantum numbers in the molecule and that the molecular binding is due to the $\pi^4\sigma$ coming from the halogen.

Replacing $4s$ and $5s$ for the above $6s$ gives possible ZnF and CdF configurations, which have now been identified, as both these molecules give the same type of atomic-like transitions. The same band systems were also sought for and found among unanalysed data in nearly all the other halides of these atoms.

Now the $^2\Pi$ and $^2\Sigma$ states thus established are not related precessionally because they derive from different l values, but the state $6s\sigma 6p\pi)\pi^4\sigma\ {}^2\Pi$ should have such a precessional state $6s\sigma 6p\sigma)\pi^4\sigma\ {}^2\Sigma$ related to it. Attention was called to the fact that in most of the halides investigated, the $^2\Pi - {}^2\Sigma$ system was mixed up with a fragmentary one having the same vibrational constants, this confusion being one of the difficulties met with in the analysis. In the case of ZnF, Rochester (1939) definitely attributed these additional bands to a $^2\Sigma - {}^2\Sigma$ transition, and there seems no doubt that his allocation is correct, in which case

* It is proposed to use the term *ground line* throughout this work in preference to " resonance line " to avoid confusion with the quantum resonance which is discussed in the text.

the upper $^2\Sigma$ state must be the $4s\sigma 4p\sigma)\pi^4\sigma\ ^2\Sigma$. The reason why such a definite statement can be made is the occurrence of the $^2\Sigma-{}^2\Sigma$ always in the same region of the atomic ground line as the $^2\Pi-{}^2\Sigma$, showing that both systems are intimately related to the atomic $^3P_1-{}^1S$ line.

The closeness of these two precessional levels $^2\Sigma$ and $^2\Pi$ to each other means that very strong resonance can be expected betwen them. Unfortunately the data on the $^2\Sigma$ state are so incomplete—in some cases its existence can only be inferred—that the difference in energy $\nu_{\pi,\Sigma}$ between the two states cannot be given. In ZnF, $^2\Sigma$ lies slightly above $^2\Pi$, whilst in the Hg halides it lies between the two $^2\Pi$ components, i.e. the separation is less than the $\Lambda-\Sigma$ coupling. In most cases it is certain that the resonance is closer than in any molecule hitherto studied. In such cases the L vector must be almost completely uncoupled from the nuclear axis. Now van Vleck's theoretical relations are only applicable to cases in which $\nu_{\pi,\Sigma}$ is large compared with the $\Lambda-\Sigma$ coupling coefficient A, and in this case this is far from being fulfilled. It can be anticipated, however, that for these precessional states the Λ-type and spin doubling will be very large and probably greater than the rotational levels themselves.

Certainly interesting results can be expected from a rotational analysis of any of these systems, but the prospects of such an analysis being made are remote because of the close structure of these heavy molecules, e.g. the $^2\Pi_{\frac{1}{2}}-{}^2\Sigma$ system of HgF is represented mainly by Q branches, each of which is condensed into quite a narrow line, but it may be possible to resolve the ZnF structure.

It is interesting to note that the fading out of the P and R branches in the above system may be a consequence of the close resonance, as well, maybe, as the diffuse appearance of the $^2\Sigma-{}^2\Sigma$ system in other cases.

§ 3. APPLICATION TO THE SPECTRA OF Ga, In AND Tl OXIDES

Isoelectronic with the halides already discussed are the molecules GaO, InO and TlO, and it is reasonable to expect a close similarity of electron configuration for these molecules. From Ga, $6s^2 6p\ ^2P$ + O, $2p^4\ ^3P$ the configuration GaO, $\sigma^2\sigma^2\pi^3$, $^2\Pi_i$ could result using molecular orbitals, but examination of the known spectra shows that a construction similar to the Hg halides must be assumed.

(a) *GaO*. This is found in a Ga arc in air and has been studied most recently by Guernsey (1934). The bands occur near the Ga ground lines $^2S-{}^2P$ (^2P separation 826 cm.$^{-1}$), most having double heads with an average separation of 2·6 cm.$^{-1}$.

These are described as R heads of a $^2\Sigma-{}^2\Sigma$ system and represented by

$$\nu = \left.\begin{matrix}25706{\cdot}43\\ 9{\cdot}04\end{matrix}\right\} + (763{\cdot}63u' - 3{\cdot}89u'^2) - (767{\cdot}69u'' - 6{\cdot}34u''^2).$$

Evidence is mentioned of a second system lying in the 4300–4900 A. region, the bands being faint and almost entirely obscured by a continuum attributed to Ga_2, but no data are given for this system.

(b) *InO*. This spectrum has been investigated by Watson and Shambon (1936), who produced it in exactly the same way as for GaO. Band heads are observed from 3847 to 4763 A., the strong ones being confined to the region of

the In ground lines $^2S-{}^2P$ (^2P separation 2122 cm.$^{-1}$) and are considered to be due to either a $^2\Pi-{}^2\Sigma$ or a $^2\Sigma-{}^2\Pi$ system. Watson and Shambon favour $^2\Pi-{}^2\Sigma$ in view of $^2\Sigma$ being apparently the ground state of GaO. Their quantum formula for this system is

$$\nu=\left.\begin{matrix}23595\cdot10\\23033\cdot10\end{matrix}\right\}+(626\cdot66u'-3\cdot40u'^2)-(703\cdot09u''-3\cdot71u''^2-0\cdot285u''^3),$$

the cubic term being necessary to cover the rapid convergence of the lower state.

There is evidence of another system interlaced within this doublet system.

§ 4. INTERPRETATION

The account of the spectra of these molecules in terms of electron configurations, which will follow, is based upon the following considerations:—

(1) The spectra, produced in the same way, belong to very similar molecules, and should, therefore, be due to the same transition, i.e. they should be both $^2\Sigma-{}^2\Sigma$ or both $^2\Pi-{}^2\Sigma$ or $^2\Sigma-{}^2\Pi$. That this is apparently not so demands an explanation.

(2) Both systems are corresponding ones in that they both occur in the region of the corresponding atomic ground lines.

(3) The vibrational frequencies are very similar in upper and lower states of both molecules.

(4) In each case there are signs of the existence of another system in the same region.

The occurrence of both spectra near the atomic ground lines suggests that, as in the Hg halides, the transition is between atomic orbitals related to the ^2S and ^2P orbits. This is borne out by the near equality of the vibrational frequencies, which is a characteristic feature of such transitions.

Now the ground state must derive from

$$\text{Ga, } 4s^2 4p\ {}^2P + \text{O, } 2p^4\ {}^3P$$

and the excited state

$$\text{Ga, } 4s^2 5s\ {}^2S + \text{O, } 2p^4\ {}^3P,$$

so that the molecular electron configurations must be

$$\text{GaO}\quad \left.\begin{matrix}4s\sigma^2\ 4p\sigma)\pi^4\ {}^2\Sigma\\ 4s\sigma^2\ 4p\pi)\pi^4\ {}^2\Pi\end{matrix}\right\}\text{ground state}$$

and the excited state

$$\text{GaO}\quad 4s\sigma^2 5s\sigma)\pi^4\ {}^2\Sigma.$$

The two possible configurations for the ground state are linked precessionally, an interesting difference from the Hg halides, where the precession states are excited. The foregoing applies also to InO by replacing $4p$ and $5s$ by $5p$ and $6s$.

The observed band systems can now be identified as

$$\text{GaO}\quad 5s\sigma)\pi^4\ {}^2\Sigma - 4p\sigma)\pi^4\ {}^2\Sigma$$

and

$$\text{InO}\quad 6s\sigma)\pi^4\ {}^2\Sigma - 5p\pi)\pi^4\ {}^2\Pi,$$

i.e. the InO system is not $^2\Pi-{}^2\Sigma$ as Watson and Shambon believed. Which of the two possible ground states is the lower is not certain, as this depends upon a more complete study of the unassigned bands mentioned in both investigations. With GaO it is certainly probable that $^2\Sigma$ is the ground state with, possibly,

the 4900 A. system, as the $^2\Sigma - {}^2\Pi$: but with InO it looks as though the resonance is so close that both states have an equal claim to be considered the ground state.

It is not at all certain that Watson and Shambon's identification of the 560 cm.$^{-1}$ interval as the $^2\Pi$ separation is correct, for this doubling is not of the expected order. This should be due entirely to the $5p\pi$ electron, and is related to the coupling factor of the $5p$ electron of In. The magnitude of the expected $^2\Pi$ splitting turns out to be 1475 cm.$^{-1}$, and in view of the strongly atom-like nature of the transition it would be unusual if the correspondence did not extend to the magnitude of the coupling.

The two levels which Watson and Shambon have linked together as $^2\Pi$ may possibly turn out to be a $^2\Sigma$ and one component of the $^2\Pi$. This $^2\Sigma$ will have vibrational constants almost identical with the $^2\Pi$, and so would fit into a doublet scheme without difficulty. It is evident that there is a need for a further experimental study of this molecule.

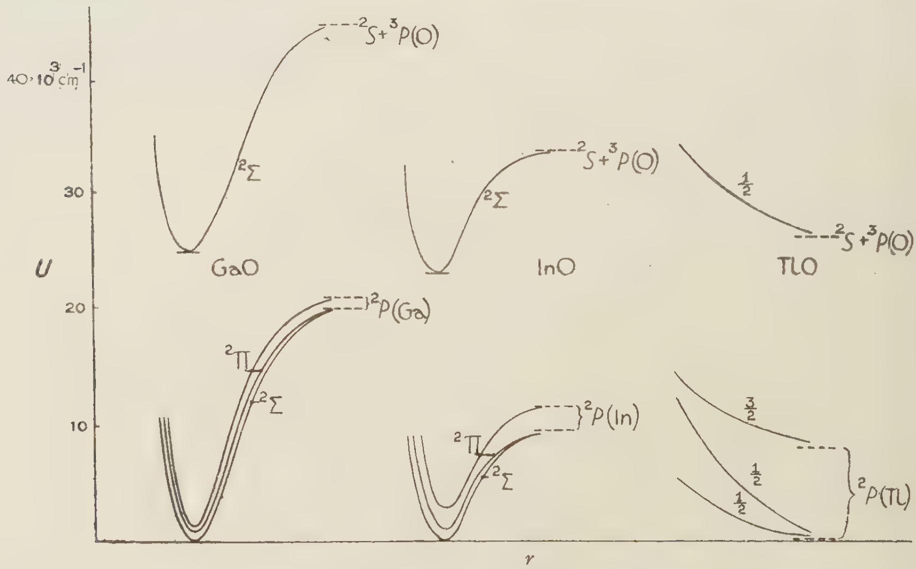
§ 5. DISSOCIATION ENERGIES AND POTENTIAL-ENERGY CURVES OF GaO, InO AND TlO

With these molecules there is no doubt as to the nature of the dissociation products, viz.:

$$^2P_{\frac{1}{2}}(\mathrm{Ga}) + {}^3P\,(\mathrm{O}) \text{ for } {}^2\Sigma \text{ and } {}^2\Pi_{\frac{1}{2}},$$
$$^2P_{\frac{3}{2}}(\mathrm{Ga}) + {}^3P\,(\mathrm{O}) \text{ for } {}^2\Pi_{\frac{3}{2}},$$
$$^2S\,(\mathrm{Ga}) + {}^3P\,(\mathrm{O}) \text{ for } {}^2\Sigma$$

and also for InO.

This fact, together with the rapid convergence of the ground state in the



Potential-energy curves for GaO, InO and TlO.

case of InO, renders it possible to calculate fairly reliable values of both D' and D'' for this molecule. This gives $D''=9000$ and $D'=11{,}000$ cm.$^{-1}$. Using direct extrapolation for the GaO ground state and assuming that a similar tendency exists for a slightly more rapid convergence than is given by the formula, a value of $D''=20{,}000$ cm.$^{-1}$ is obtained. This gives $D'=19{,}000$ cm.$^{-1}$, which

shows that in both molecules both states have practically the same D values, and hence almost identical potential-energy curves. These are sketched in the figure, assuming $^2\Sigma$ to be the lowest in each case.

Watson and Shambon report that they found no bands in the Tl arc in air in the neighbourhood of the Tl ground lines, and concluded that one or both of the corresponding TlO levels were unstable. That this is probably the case can be inferred from the big reduction in stability in going from GaO to InO (20,000 to 9000 cm.$^{-1}$). Since there is a large increase in the weight of the TlO molecule, there seems little chance that any of the levels will have even a flat minimum in their potential-energy curves. The probable course of these is sketched in the figure, assuming that a case-c coupling tendency is marked with this heavy molecule, and so each level is represented by its Ω value.

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THE SPECTRA OF TIN AND LEAD HYDRIDES

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ABSTRACT. It is shown that the $^2\Pi$ ground-state doubling of SnH is due to a $p\pi$ electron, and its magnitude can be predicted from the ^3P width of the Sn ground state. The same doublet separation is found among the red bands of SnH, and a vibrational analysis is presented for this system, which is considered to be a $^2\Sigma-{}^2\Pi$. It is assumed that PbH will also have a $^2\Pi$ ground state with an estimated separation of 8200 cm.$^{-1}$ and which is modified by case-c coupling. Although this interval is actually found among the PbH bands, its occurrence is not taken as proof of the existence of the $^2\Pi$ ground state, as it appears to be more likely the separation of two excited states. The red system analysed by Watson and Simon and described by them as $^2\Sigma-{}^2\Sigma$ is here interpreted as a $\frac{1}{2}(^2\Sigma)-\frac{1}{2}(^2\Pi)$ system analogous to the SnH $^2\Sigma-{}^2\Pi$ system, and an isolated band at 3815 A. is considered to be the 0,0 band of $\frac{3}{2}(^2\Delta)-\frac{1}{2}(^2\Pi)$. It is explained why the main band system has the appearance of a $^2\Sigma-{}^2\Sigma$ system and why the spectra of SnH and PbH are apparently so dissimilar.

The occurrence of two GeH systems is predicted. A similarity between the hydrides and halides of this carbon group is described and a number of $^2\Pi$ separations for the ground states of these molecules is predicted.

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§1. INTRODUCTION

The spectrum of lead hydride, PbH, has been investigated by Watson (1938) and by Watson and Simon (1940), using a high-pressure arc in hydrogen. They found bands extending from 5000 A. to 9100 A., apparently belonging to one system which, after a rotational analysis had been made, was

considered to be a $^2\Sigma - ^2\Sigma$. This conclusion was reached even though some of the bands had branches whose intensities seemed out of order for such a transition and which favoured rather a $^2\Pi - ^2\Pi$ transition. This latter possibility was finally dismissed, owing to the absence of the expected sub-bands and of certain combination differences.

The same workers (1939) have also studied tin hydride, SnH, using the same method of excitation, and they identified bands at 4054 and 4447 as belonging to a $^2\Delta - ^2\Pi$ system with a normal $^2\Pi$ state ($A = 2183$ cm.$^{-1}$) and an inverted $^2\Delta$ with a very small splitting ($A = -1{\cdot}75$ cm.$^{-1}$). In addition, weaker bands were found in the red, but a satisfactory analysis of these could not be made. The only bands listed were at 6745, 6892, 7032 with a pile-up of lines at 6931 and also at 6095 and 6214 A. A certain number of $^2\Pi$-state combination differences were found among lines around 6931, and Watson and Simon consider that these bands probably belong to a $^2\Sigma - ^2\Pi$ transition, as they are quite different from the bands of the red $^2\Sigma - ^2\Sigma$ system of PbH.

The surprising feature of this comparison of these two molecules is the complete lack of any similarity between their spectra. An attempt to obtain the analogous $^2\Delta - ^2\Pi$ system of PbH was actually made by Watson and Simon, but they found only a weak band at 3815 A. which was " not accompanied by another at any plausible interval for a $^2\Pi$ PbH state ". This lack of correspondence is surprising in view of the close resemblance of tin and lead, which in the author's opinion is sufficient to guarantee a similarity of electron configuration in corresponding molecules. The common mode of excitation and the need for high pressures in both cases suggest that the same type of electronic levels is involved. It is particularly difficult to interpret the $^2\Sigma - ^2\Sigma$ system of PbH in terms of electron configurations. Watson and Simon accounted for these levels by assuming that they are formed from Pb, $6p^2$ + H, $1s$, the latter being promoted to a $7s$ orbit to give $6p\sigma^2 7s\sigma\, ^2\Sigma$ and $6p\pi^2 7s\sigma\, ^2\Sigma$. Such a transition involves a two-electron jump, and one cannot but feel uneasy over such an explanation, particularly in view of the absence of any normal transition. The levels normally expected would be $6p\sigma^2 6p\pi\, ^2\Pi$ and $6p\sigma 6p\pi^2\, ^2\Delta$, $^2\Sigma^+$, $^2\Sigma^-$, all of which are found in CH.

The difference in spectral types in SnH and PbH therefore presents a problem which it is hoped this paper will solve. It will be shown that there are actually points of resemblance between them, and that the observations of Watson and Simon can be included within a consistent scheme. In particular, an alternative interpretation of the red $^2\Sigma - ^2\Sigma$ bands will be given and an analysis of the red SnH bands will be suggested.

§ 2. COMPARISON WITH SIMILAR HYDRIDE MOLECULES

Much can often be learnt and predicted about the various band systems of a molecule by comparing them with the well-established systems of a similar molecule. By *similar molecules* are meant those in which one atom is common, whilst the others belong to the same group of the Periodic Table. This is different from the "similarity" of iso-electronic molecules such as N_2 and CO, and it is proposed to differentiate by calling the similar molecules here discussed *group molecules*. Thus, in the present case the molecules SnH and PbH will

be compared with their group molecules CH, SiH and GeH. However, as yet nothing is known about GeH, and so we are restricted to CH and SiH. CH has a $^2\Pi$ ground state with a doublet separation of 28·5 cm.$^{-1}$ with $^2\Delta$, $^2\Sigma^+$ and $^2\Sigma^-$ in that energy order. SiH also has a $^2\Pi$ ground state with the larger separation of 124 cm.$^{-1}$, and the only known excited state is the corresponding $^2\Delta$. Thus, assuming a close similarity between group molecules, the $^2\Pi$ state of SnH can be safely identified as the ground state and a similar level with a still larger separation

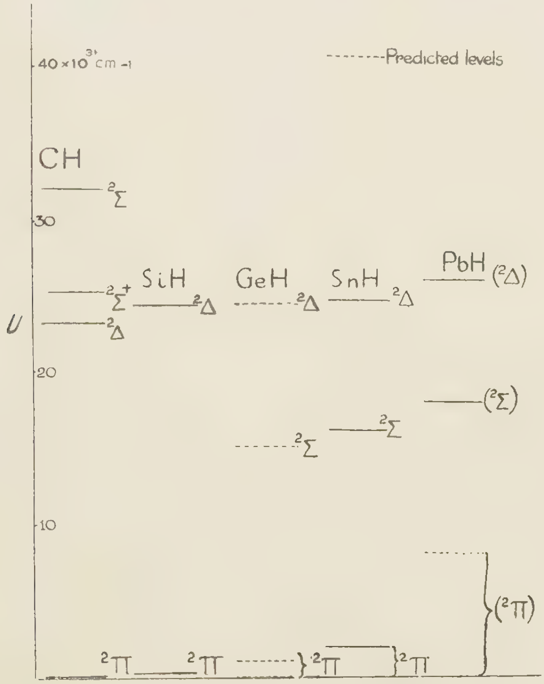

Figure 1. Energy levels of CH-type group molecules

can be expected to be the ground state of PbH. In figure 1 are collected all the known states of these molecules together with predicted states which will be described in due course. An obvious line of enquiry lies in the investigation of the $^2\Pi$ separations with the aim of predicting that expected for a PbH state. Another is to explore the possibility of other states competing with the $^2\Pi$ for the ground state. There seems no likelihood of this in CH or SiH, nor is any such state predicted from a study of the electron configurations.

§ 3. RELATION BETWEEN ATOMIC AND MOLECULAR COUPLING FACTOR

The author showed that with HgF and its group molecules the atomic coupling factor *a* of the outer *p* electrons was related to the coupling coefficient *A* of the molecule which determines the $^2\Pi$ separation (1943). This relation indicated that the atomic *p* electron became a $p\pi$ in the molecule, and it enabled the $^2\Pi$ separation to be determined for a number of these molecules whose spectra had remained unanalysed. By using the predicted interval as base, it was found possible to present satisfactory analyses. In the present case

the doubling in the $^2\Pi$ state is due to a single π electron, and it is possible that a similar relation holds. The doublet separation should be equal to the atomic coupling coefficient a of the corresponding p electron. Table 1 gives these a values and the $^2\Pi$ interval $\Delta\nu$ where known.

Table 1. Comparison of a (from ^3P) with $^2\Pi$ interval

	CH	SiH	GeH	SnH	PbH
a (calc.)	28	149	940	2285	7800*
$^2\Pi$ (observed)	29	124	—	2183	8200†

* From a of Pb^+ (^2P). † Independent estimate.

Neglecting PbH for the moment, it can be seen that the agreement for CH, SiH and SnH is sufficient to confirm the view that here too the p electron definitely becomes a $p\pi$ electron. Further, the agreement for SnH seems a justification for expecting an equally good correspondence for PbH, and encourages the view that the $^2\Pi$ interval for this molecule can be predicted. Now the value of a cannot be determined directly from the $6p^2\,{}^3P$ width of the Pb ground state as in the other cases, as the separation of the ^3P components shows a big departure from normal L–S coupling. It is, however, possible to estimate the value from $6p\,{}^2P$ of Pb^+, as comparison of the a values derived from Si and Si^+ and Sn and Sn^+ reveals that the ionized atom gives a value 28 % and 23 % too high for Si and Sn respectively, and so, assuming that a from Pb^+ will be 20 % too high, a value of 7820 cm.$^{-1}$ is obtained. That this is probably on the low side is indicated by an independent method to be described later, which gives a value of 8230 cm.$^{-1}$ for the doublet width of $^2\Pi$.

The observation that with Pb a radical change of coupling has taken place is significant, for it means that if a change of term type does occur with any member of this molecular group, it should take place with PbH, for any change in the atomic constitution should be reflected in the molecule.

It begins to appear, therefore, that differences are to be expected in the PbH spectrum. This does not mean that the problem has been removed, for it is still necessary to interpret the apparent $^2\Sigma$, $^2\Sigma$ states and to explain how they have changed from the expected $^2\Delta$ and $^2\Pi$. It is probable that such a change has come about by alterations in the type of coupling, but it should always be possible to trace this change and to correlate the observed levels with those expected for normal coupling. Before this is done it will be found advantageous to clear up the explanation of the red bands of SnH.

§4. THE RED SYSTEM OF SnH

By the number of observed branches and the occurrence of some combination differences among a few of the red bands of SnH, a $^2\Sigma-{}^2\Pi$ transition was suspected by Watson and Simon. Assuming that $^2\Pi$ is the ground state, it follows that, unless only one component of the doublet is present, there must occur the ground-state interval of 2183 cm.$^{-1}$ among these bands. Of the five listed, two do show such a difference, viz. 6095 A. and 7030 A., which have a

separation of 2181 cm.$^{-1}$, which seems too close to the expected value to be a coincidence. Assuming these to be the 0,0 bands of the system, they can be arranged in the following vibrational scheme:—

Table 2. Vibrational scheme for red bands of SnH

v'' \ v'	0		1
0	16402 2181 14221		
	(1580)		
1	14822	(1266)	16088
			(1582)
2			14506

The missing members of the $^2\Sigma - {}^2\Pi_{\frac{3}{2}}$ system should lie to the red of the last measured band, 7030 A., and Watson and Simon mention that more bands do lie to the red of this. There should also be members of the $\Delta v = 1$ sequence found on over-exposed plates. If this arrangement is accepted, then ω_e'' and ω_e' are approximately 1600 and 1300 cm.$^{-1}$ respectively. Although the value of ω_e'' cannot be checked from the $^2\Delta - {}^2\Pi$ system (as this is limited to the 0,0 bands) it is of the right order, as it should be between the value of 2000 for SiH and 1560 cm.$^{-1}$ for PbH, and necessarily nearer to the latter, since another value, that of GeH, must intervene. This assumes that the value quoted refers to the ground state of PbH. To complete this brief account of the SnH spectrum, it remains to note that according to the probable electron configuration of the $^2\Delta$ state, it should be normal, and so it is probable that the small negative value observed for A is due to the interaction of the s of other electrons with the l of the valence electron.

§ 5. INTERPRETATION OF THE PbH SPECTRUM

If it be assumed that the ground state of PbH is $^2\Pi$, then a separation of the order of 8200 cm.$^{-1}$ ought to be found in the spectrum. That such a difference does occur has been overlooked by Watson and Simon. This is between the system origin of the red bands and the solitary band at 3815 A., and amounts to 8187 cm.$^{-1}$. This is so close to the expected value that it is tempting to conclude that the existence of the supposed $^2\Pi$ ground state is fully established, and that PbH is quite similar to its group molecules. If this is so, it remains to decide whether the upper state is $^2\Sigma$ or the expected $^2\Delta$, and then to enquire why the lower state behaves like a $^2\Sigma$.

A case can be made out for $^2\Sigma$ or $^2\Delta$, or even for both together, being the upper state of the red bands, on the hypothesis that PbH has a partial case-c coupling.

For pure case-c, the components $^2\Delta_{\frac{5}{2}}$ and $^2\Delta_{\frac{3}{2}}$ will give rise to the levels $\Omega=\frac{5}{2}$ and $\frac{3}{2}$, which can combine with the case-c ground levels derived from $^2\Pi$. This should result in an increase in the number of systems as compared with SnH. If, however, the coupling is only partial case-c, then those transitions governed by $\Delta\Omega=0$ will be favoured and others may be too weak for observation. Thus transitions $\frac{3}{2}(^2\Delta)-\frac{3}{2}(^2\Pi)$, $\frac{5}{2}(^2\Delta)-\frac{3}{2}(^2\Pi)$ and $\frac{3}{2}(^2\Delta)-\frac{1}{2}(^2\Pi)$ would be expected, among others, for pure case-c, but for partial case-c the first would be the most intense. Tentatively identifying the red system as $\frac{3}{2}-\frac{3}{2}$, the weak band at 3815 A. can be described as $\frac{3}{2}-\frac{1}{2}$, whilst $\frac{5}{2}-\frac{3}{2}$ can be assumed to be similarly weak and covered by the stronger red system. Now a case-c $\frac{3}{2}-\frac{3}{2}$ system will have a structure similar to a $^2\Pi_{\frac{3}{2}}-{}^2\Pi_{\frac{3}{2}}$, which, apart from the lowest J values, will resemble a $^2\Sigma-{}^2\Sigma$ transition. Such a view would account for the observed $^2\Sigma-{}^2\Sigma$ system, with the exception of one important detail—the so-called spin doubling of the lower state, which was found to be proportional to $K+\frac{1}{2}$. This must now be accounted for as Ω-type doubling and should be proportional to $(J+\frac{1}{2})^2$. Another difficulty is found on a closer comparison with SnH. The main system is limited to the 0,0 bands, and the 3815 PbH band $\frac{3}{2}(^2\Delta)-\frac{1}{2}(^2\Pi)$ is similarly isolated, which makes it hard to understand why the other component is represented by such a comparatively prolific number of bands. Since the red SnH system $^2\Sigma-{}^2\Pi$ has more bands than the $^2\Delta-{}^2\Pi$ (due probably to the shift of the upper potential-energy curve to larger r values) an alternative interpretation of the PbH spectrum is suggested. This is to associate the red system with a corresponding $^2\Sigma$ level (case-c $\frac{1}{2}$). The transition $\frac{1}{2}\,(^2\Sigma)-\frac{1}{2}(^2\Pi)$ will be similar to a $^2\Pi_{\frac{1}{2}}-{}^2\Pi_{\frac{1}{2}}$ transition, which again resembles a $^2\Sigma-{}^2\Sigma$, and furthermore the Ω-type doubling will now be proportional to $J+\frac{1}{2}$, which satisfies the observations of Watson and Simon. It should be recalled at this stage that the branch intensities of certain bands were in keeping with a possible $^2\Pi-{}^2\Pi$ transition. Further support for this new interpretation is obtained from figure 1, where it is seen that the $\frac{5}{2}$, $\frac{3}{2}$ $(^2\Delta)$ level in PbH is slightly higher than the corresponding level in SnH (actually 1606 cm.$^{-1}$). This difference is probably related to the difference in the atomic ionization potentials: Pb, 7·38 volts − Sn, 7·30 volts = 650 cm.$^{-1}$. Assuming a similar difference in the $^2\Sigma$ type levels, that for PbH would be expected to occur at 18060 cm.$^{-1}$, which is practically the value of ν_e for the red system. In this case the observed 8200 cm.$^{-1}$ separation is not due to the $^2\Pi$ at all, but represents the difference between $\frac{1}{2}(^2\Sigma)$ and $\frac{3}{2}(^2\Delta)$. This coincidence does not invalidate the previously developed argument for PbH having a case-c equivalent $^2\Pi$ ground state with a doubling of the order given, as the evidence given in table 1 is considered conclusive. On this view, then, the main red system is a $\frac{1}{2}(^2\Sigma)-\frac{1}{2}(^2\Pi)$ transition and the 3815 cm.$^{-1}$ band is $\frac{3}{2}(^2\Delta)-\frac{1}{2}(^2\Pi)$. The $\frac{3}{2}(^2\Delta)-\frac{3}{2}(^2\Pi)$ component ought to lie in exactly the same region as the red system because of the ground-state separation of about 8000 cm.$^{-1}$. It is rather tempting to consider that there might be two systems here, and Watson and Simon actually thought this a possibility because of the smallness of ω_e'. Its value is only half of what it should be according to the Mecke rule ω/B = constant, which could only be satisfied by assuming the

existence of two separate systems which take the alternate v' values of the system as actually analysed by Watson and Simon. They decided against this, and the author agrees with their decision on the grounds that the similarity with SnH indicates that the system should be represented by only a weak and single band which is probably masked by the main system. The exact value of the ground-state separation is then left undetermined, but it can be measured, according to this interpretation, from the position of the $\frac{1}{2}(^2\Sigma)-\frac{3}{2}(^2\Pi)$ system, whose 0,0 band ought to lie at about 10,000 A., which is more than 1000 A. further than the limit reached by Watson and Simon. Of course in true case-c coupling a $^2\Pi$ separation has no meaning, but in partial case-c the levels $(\frac{1}{2})$ and $(\frac{3}{2})$ should have a separation which is related to that which would occur for good Λ-Σ coupling.

§6. POTENTIAL-ENERGY CURVES AND DISSOCIATION ENERGY OF PbH

In figure 2 is sketched the probable course of the potential-energy curves of the PbH states involved in this paper. They are all the case-c equivalents of those levels arising from the electron configurations $6p\sigma^2 6p\pi$, $^2\Pi$ ground state and $6p\sigma 6p\pi^2$ $^2\Delta$, $^2\Sigma^+$, $^2\Sigma^-$. Direct extrapolation of the vibrational levels of the

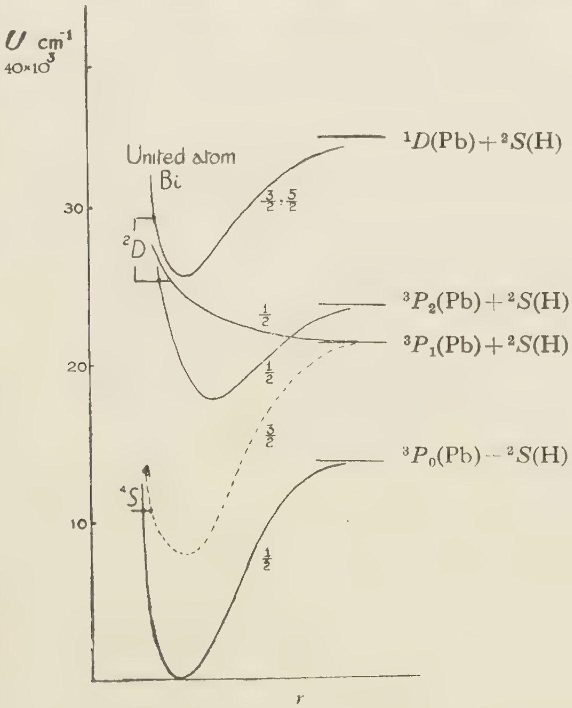

Figure 2. Potential-energy curves for PbH.

ground state gives $D'' = 18{,}000$ cm.$^{-1}$, which is probably an over-estimate, and so a value of 14,000 cm.$^{-1}$ has been chosen.

The ground state dissociates into $^3P_0(\mathrm{Pb})+{}^2S(\mathrm{H})$ and the $\frac{3}{2}$ level into $^3P_1+{}^2S$, which fixes D' for the $\frac{3}{2}$ state at about the same value as D''. The

upper level $\frac{1}{2}$ of the red system must give $^3P_2$(Pb) on dissociation to account for its stability and also for the intersection by the curve responsible for its predissociation. According to Watson and Simon, this takes place at a point 3200 cm.$^{-1}$ above the $v'=0$ level, i.e. at about 21,200 cm.$^{-1}$, in good agreement with the value of the asymptote of the $\frac{3}{2}$ level, 22,000 cm.$^{-1}$. This repulsive level must be a $\frac{1}{2}$ level, as $^3P_1+{}^2S$ can only give one $\frac{3}{2}$ state, and this has already been accounted for.

The remaining unresolved levels, $\frac{3}{2}$ and $\frac{5}{2}$, must dissociate into ^1D (Pb) and have a D value of about 9200 cm.$^{-1}$. All the levels in the figure are probably correlated with the states ^4S and ^2D of the united atom Bi as shown.

§ 7. THE GeH SPECTRUM

Although no study has yet been made of the GeH spectrum, a comparison with the molecules lying on each side of GeH in figure 1 enables the following predictions to be made about it:—

(*a*) Its $^2\Pi$ ground state should have a doublet separation of about 920 cm.$^{-1}$ —estimated from the ^3P ground state of Ge, and also by another method to be described in the next section.

(*b*) The $^2\Delta-{}^2\Pi$ system should be the strongest, the $^2\Delta$ level lying midway between the $^2\Delta$ for SiH and SnH at 24,400 cm.$^{-1}$ This places the 0,0 bands at about 4100 A. and 4260 A.

(*c*) The ground state ω'' value should be about 1700 cm.$^{-1}$.

(*d*) The problem of the $^2\Sigma$ state is somewhat more difficult to settle. No such state has as yet been observed in SiH, but its appearance in SnH suggests that it probably exists in GeH, particularly as Ge is perhaps more closely related to Sn than to Si. Its position is then probably as in figure 1, at about 16,000 cm.$^{-1}$.

§ 8. DOUBLET SEPARATIONS IN HYDRIDES AND HALIDES

It has been established that the ground state of the PbF halide-type group molecules is $^2\Pi$, and the doublet separation has been determined in a number of cases. These are shown in table 3 along with the corresponding hydride

Table 3. $^2\Pi$ separations of CH and CF group type molecules

	a	H	F	Cl	Br	I
C	28	29	(60)	96	(150)	(250)
Si	149	124	161	208	408	(600)
Ge	940	(920)	(940)	975	1150	(1400)
Sn	2285	2183	2317	2360	2467	(2600)
Pb	7800	(8200)	8266	(8310)	(8450)	(8600)

(predicted value)

value, and also the *a* value of the atomic *p* electron, which is certainly involved in the case of the hydride. It will be noticed that the hydride seems to belong to the same family of group molecules as the halides, in which the separation increases as the molecule gets bigger. This is understandable in terms of electron configurations, for the extra eight electrons of the F atom can easily form closed shells in the molecule, leaving the odd one to occupy the same type of orbital as in the hydride.

From the observed separation of 8266 cm.$^{-1}$ for the $^2\Pi$ ground state of PbF, a reasonable value of about 8230 cm.$^{-1}$ seems likely for PbH. This is how the value given in table 1 for PbH was estimated. In the same way, assuming the same general increase in the separation from C to Pb as each halide increases in weight, all the values enclosed in brackets in table 3 have been determined. That for GeH has been compared with the 940 cm.$^{-1}$ obtained from the L–S coupling coefficient of Ge ^3P. and the mean value of 920 cm.$^{-1}$ was used in the discussion on GeH in the previous section. The predicted separations in table 3 are obviously more reliable for the hydrides and fluorides than those for the other halides.

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A PROBLEM OF HEAT CONDUCTION WITH SPHERICAL SYMMETRY

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ABSTRACT. Solutions are given for a problem in heat conduction through two concentric spheres, suggested by the heating up of a body in a furnace. Exact solutions are given, and also simple approximate solutions which will often be applicable in practice.

§ 1. INTRODUCTION

The problem is suggested by the heating up of a body placed at the centre of a furnace cavity. The system considered consists of a conducting sphere of radius *a* concentric with a spherical cavity of radius *b*, the annular space being filled by a conducting medium. The outside surface of the cavity is maintained at a fixed temperature, taken arbitrarily as zero, and the initial temperature of the sphere is v_0. In practice, the initial temperature

of the annular space will be somewhere between v_0 and zero. We shall give results for these two extreme cases, which will be referred to as assumptions A and B respectively.

The following notation is employed:—

Index 1 refers to $0<r<a$,
Index 2 refers to $a<r<b$,
K = thermal conductivity, c = specific heat, ρ = density,
$\kappa=K/c\rho$ = diffusivity, $\mu=(\kappa_2/\kappa_1)^{\frac{1}{2}}$, $\sigma=K_2/K_1\mu$, $u=vr$.

The equations to be solved are then

$$\frac{\partial u_1}{\partial t}=\kappa_1\frac{\partial^2 u_1}{\partial r^2},\qquad \frac{\partial u_2}{\partial t}=\kappa_2\frac{\partial^2 u_2}{\partial r^2},\qquad\ldots\ldots(1)$$

subject to the continuity conditions

$$u_1=u_2,\quad K_1\left(a\frac{\partial u_1}{\partial r}-u_1\right)=K_2\left(a\frac{\partial u_2}{\partial r}-u_2\right)\quad\text{at } r=a\qquad\ldots\ldots(2)$$

and the initial and boundary conditions

$$\left.\begin{array}{llll} u_1=0, & r=0; & u_2=0, & r=b; \\ u_1=v_0r, & t=0; & u_2=v_0r \text{ (assumption A)}, & t=0; \\ & & \text{or } u_2=0 \text{ (assumption B)}, & t=0. \end{array}\right\}\qquad\ldots\ldots(3)$$

§ 2. GENERAL SOLUTION

The derivation of the solutions will not be given: they were obtained by the usual Fourier method, and in most cases checked by the Laplace transformation method. The exact solutions are:—

Assumption A:

$$v_1=\frac{2\sigma b v_0}{r}\sum_{n=1}^{\infty}\frac{\sin\mu\alpha_n a\sin\alpha_n(b-a)\sin\mu\alpha_n r\,e^{-\kappa_2\alpha_n^2 t}}{\mu\alpha_n a\sin^2\alpha_n(b-a)+\sigma\alpha_n(b-a)\sin^2\mu\alpha_n a+\dfrac{\mu\sigma-1}{\mu\alpha_n a}\sin^2\mu\alpha_n a\sin^2\alpha_n(b-a)};$$

Assumption B:

$$v_1=\frac{2av_0}{r}\sum_{n=1}^{\infty}\frac{\sin^2\alpha_n(b-a)\left\{\dfrac{1}{\mu\alpha_n a}\sin\mu\alpha_n a-\cos\mu\alpha_n a\right\}\sin\mu\alpha_n r\,e^{-\kappa_2\alpha_n^2 t}}{\mu\alpha_n\sin^2\alpha_n(b-a)+\sigma\alpha_n(b-a)\sin^2\mu\alpha_n a+\dfrac{\mu\sigma-1}{\mu\alpha_n a}\sin^2\mu\alpha_n a\sin^2\alpha_n(b-a)},\qquad\ldots\ldots(4)$$

where α_n is the nth positive root of the equation

$$\sin\alpha(b-a)\{\mu\alpha a\cos\mu\alpha a-\sin\mu\alpha a\}+\mu\sigma\sin\mu\alpha a\{\alpha a\cos\alpha(b-a)+\sin\alpha(b-a)\}=0\qquad\ldots\ldots(5)$$

The solution above is complete only if $\mu a/(b-a)$ is irrational. If $\mu a/(b-a)=p/q$, where p and q are integers, then equation (5) admits roots such that $\alpha\mu a$ and $\alpha(b-a)$ are integral multiples of π, and the corresponding terms (which are limiting forms of those already given) take the forms:

Assumption A:

$$-\frac{2b\sigma v_0}{\pi r(p\sigma+q)}\sum_{s=1}^{\infty}\frac{(-)^{(p+q)s}}{s}\sin\frac{ps\pi r}{a}\exp.\left\{-\frac{s^2p^2\pi^2}{\mu^2a^2}\kappa_2 t\right\};$$

Assumption B:

$$-\frac{2a\sigma v_0}{\pi r(p\sigma+q)}\sum_{s=1}^{\infty}\frac{(-)^{sp}}{s}\sin\frac{ps\pi r}{a}\exp.\left\{-\frac{s^2p^2\pi^2}{\mu^2a^2}\kappa_2 t\right\}. \qquad \ldots\ldots(6)$$

The problem corresponding to assumption A has previously been treated by Carslaw (1920) in connection with the rate of cooling of the earth's crust. Allowing for differences in notation, his formula for the additional terms agrees with our equation (6 A), but his version of (4 A) has an incorrect denominator, which is not of the right physical dimensions.

§ 3. PARTICULAR CASES

For practical purposes these equations can often be considerably simplified. Thus, if the central sphere is a sufficiently good conductor, the temperature inside $r=a$ can be taken as uniform, i.e. v_1 is independent of r. Under these conditions the second continuity condition in equation (2) is replaced by

$$3K_2\frac{\partial v_2}{\partial r}=ac_1\rho_1\frac{\partial v_1}{\partial t}\quad\text{at } r=a. \qquad \ldots\ldots(7)$$

This leads to the following equations:

Assumption A:

$$v_1=\frac{6v_0b}{a}\sum_{n=1}^{\infty}\frac{\sin\alpha_n(b-a)e^{-\kappa_2\alpha_n^2t}}{2\frac{\mu}{\sigma}\alpha_n a\sin^2\alpha_n(b-a)+3\alpha_n(b-a)-\frac{3}{2}\sin 2\alpha_n(b-a)};$$

Assumption B:

$$v_1=2v_0\sum_{n=1}^{\infty}\frac{\alpha_n a\sin^2\alpha_n(b-a)e^{-\kappa_2\alpha_n^2t}}{2\alpha_n a\sin^2\alpha_n(b-a)+3\frac{\sigma}{\mu}\{\alpha_n(b-a)-\frac{1}{2}\sin 2\alpha_n(b-a)\}}, \qquad \ldots\ldots(8)$$

where α_n is now the nth positive root of the equation

$$\alpha_n a\cot\alpha_n(b-a)+1=\tfrac{1}{3}\frac{\mu}{\sigma}\alpha_n^2a^2. \qquad \ldots\ldots(9)$$

In this case there are no terms analogous to (6). It may be noted that when $a=0$, (8 B) reduces to

$$v_1=2v_0\sum_{n=1}^{\infty}(\mp)^n e^{-\frac{n^2\pi^2}{b^2}\kappa_2 t}, \qquad \ldots\ldots(10)$$

agreeing with the well-known result for the temperature at the centre of a sphere, the surface of which is held at a constant temperature.

In the practical problem of a body heating up in a furnace, it is often the later stages of the process which are of interest; for example, we may wish to

know what time is necessary for the whole of the body to reach the furnace temperature within certain limits of error. Under these circumstances it is a good approximation to take only the first term of equation (4) or (8), and the additional terms in (6) are negligible. Moreover, for the later stages it is easy to find the conditions under which it is legitimate to assume a uniform temperature within the sphere $r=a$. If v_c and v_a are respectively the temperatures at the centre and surface of the sphere in the later stages, then equations (4) and (5) give (for both assumptions A and B)

$$1-\frac{v_a}{v_c}=1-\frac{\sin\mu\alpha_1 a}{\mu\alpha_1 a}\leqslant\tfrac{1}{2}\sigma\mu\frac{b}{b-a}. \qquad \text{......(11)}$$

The condition for using the first term of (8) rather than the first term of (4) is thus $\frac{1}{2}\sigma\mu b/(b-a)\ll 1$. Finally, if the following conditions hold simultaneously,

$$\tfrac{1}{2}\sigma\mu\frac{b}{b-a}\ll 1, \quad \frac{3\sigma}{\mu}\cdot\frac{b(b-a)}{a^2}\ll 1, \qquad \text{......(12)}$$

then either assumption A or assumption B gives the following very simple formula for the later stages:

$$v_1=v_0\exp.\left\{-\frac{3\sigma}{\mu}\cdot\frac{b}{a^2(b-a)}\kappa_2 t\right\}. \qquad \text{......(13)}$$

Equation (13) will often be applicable in practice, especially if a high accuracy is not needed. The proportional errors in the times which it predicts for a given value of v_1/v_0 will be of the same order of magnitude as the two quantities in equation (12). Equation (13) will also give approximate values for non-spherical systems, provided that average values of $b/a^2(b-a)$ are taken.

If the furnace temperature is high and the annular space wide, heating by radiation may be more important than heating by conduction. If the temperature inside the sphere is effectively uniform, then heating by radiation alone would give

$$v_1=v_0 e^{-3Et/ac_1\varrho_1}, \qquad \text{......(14)}$$

where the emissivity E can be estimated from the Stefan radiation constant and the absolute temperature of the formula. The result for non-uniform temperature inside the sphere has been given by Awbery (1927) in connection with the cooling of apples in refrigerators.

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COLORATION AND LUMINESCENCE PRODUCED BY RADIUM RAYS IN THE DIFFERENT VARIETIES OF QUARTZ, AND SOME OPTIC PROPERTIES OF THESE VARIETIES

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ABSTRACT. Systematic studies of the coloration and luminescence produced by radium rays, on the one h nd, and of the absorption spectra and ultra-violet transparency on the other, have been made on four varieties of quartz, namely, the colourless, the smoky, the citrine and the rose, in their crystalline and vitreous states. The chief results may be summarized as follows:—(1) After being exposed to the irradiation of the β and γ rays of radium, the crystals of all four varieties of quartz turn to different shades of black, so that in appearance they resemble very smoky quartz. The persistence of the coloration under heat treatment depends, however, on the variety. (2) The same rays render vitreous quartz of the four varieties violet in colour instead of smoky. (3) Under the influence of radium rays, all the specimens of quartz, crystalline and vitreous, fluoresce and thermo-phosphoresce in bluish-green or bluish-white light, with the sole exception of crystalline rose quartz, which emits orange light. (4) Under heat treatment, coloration and thermo-phosphorescence do not disappear simultaneously, the latter being more persistent. (5) Complementary observations with the use of X rays and ultra-violet radiations have shown that the coloration and the luminescence caused by X rays are exactly the same as those produced by the radium rays, and that the ionizing ultra-violet radiations have a very marked decolourizing effect on the smoky quartz, but have no similar effect on the artificial violet colour of vitreous quartz. (6) Among the naturally and artificially coloured specimens of quartz, the violet vitreous quartz is the only one which possesses a band structure in its ultra-violet absorption spectrum. (7) In passing from the naturally colourless quartz to the three decolourized varieties, the limit of ultra-violet transparency recedes from $\lambda=1850$ A. to the vicinity of $\lambda=2250$. Among the decolourized specimens of the three coloured varieties, crystalline and vitreous quartz of the smoky variety are the most transparent and the rose variety the least.

Certain discrepancies, concerning the coloration and luminescence of quartz, between the present results and those of previous workers are pointed out and discussed.

§ 1. INTRODUCTION

THE coloration and luminescence of quartz produced by the rays of radium have already been the subject of study by several investigators, notably A. Bensaude and G. Costanzo (1922), S. C. Lind and D. C. Bardwell (1923), and J. Hoffmann (1931). Their work was mainly limited to the observations of the effects produced either on colourless quartz (crystalline and vitreous) or on certain coloured crystalline quartzes. Since the phenomena of coloration and luminescence produced in quartz are, as in other transparent minerals,

complicated in nature, it seems necessary to follow closely the variations of these phenomena with the physical states of the quartz, and also of the impurities it contains, in order that a better understanding may be acquired. In addition, a knowledge of certain thermal and optical properties of the coloured and luminescent substances appears also to be essential. It was such considerations as these that led the writer to study systematically (1) the effects of coloration and luminescence caused by the radium rays in different varieties of quartz, both crystalline and vitreous, and (2) the spectroscopic properties of quartz before and after heating, using both naturally coloured specimens and others artificially coloured by radium rays. With a view to comparing such effects with those caused by other kinds of rays, some complementary observations, with the use of X rays and ultra-violet radiations as exciting sources, have also been carried out.

§ 2. EXPERIMENTAL

Four varieties of quartz, namely, the colourless, the smoky, the citrine, and the rose, were used in the investigation. The specimens of vitreous quartz of each variety were prepared by fusing the corresponding crystals in a gas-oxygen flame.

50 mg. of radium contained in a platinum tube, of which the wall was 0·5 mm. in thickness, were used in the experiments. Owing to the absorption of the tube wall, it is certain that the colouring and luminescent effects observed are due entirely to the external-conversion β rays and the penetrating γ rays. The α rays, and almost all of the β rays, emitted directly from the radium and its derivatives are stopped by the wall of the tube. The specimens of quartz to be irradiated were placed on the radium tube. The time of irradiation varied from 30 to 50 days.

As the source of X rays, a Roentgen tube with copper anode and aluminium-foil window was used; at a voltage of 50 kv. and a current of 10 ma., the time of exposure was 4 hours.

The ultra-violet radiation used for the study of the colouring and luminescent effects, and also for the study of absorption spectra of the specimens of coloured quartz, was furnished by a hydrogen discharge tube. This tube, which had a power of about 1 kw., was closed at one end by a quartz window and at the other end by a fluorite window. The specimen to be irradiated was put in contact with one of these windows, in order to minimize the loss of radiations of short wave-length due to air absorption. The extent of the spectral region used could be varied according to the kind of window with which a specimen was placed in contact.

A large quartz spectrograph of the Littrow model was used for the study of the absorption spectra and a fluorite vacuum spectrograph for the comparison of the transparency limits of the colourless and decolourized specimens. The spark spectrum of silver was used for this comparison.

The photographic plates used for the ultra-violet region of short wave-lengths were ordinary plates sensitized with sodium salicylate, according to the process described by J. Terrien (1936).

§ 3. RESULTS

(a) *Coloration*

When a specimen of quartz a few mm. in thickness is exposed to the rays of radium, the part of its surface in contact with or near the radium tube becomes rapidly coloured. Evidently this is due to β rays, which are known to be much more effective in colouring and much less penetrating than the γ rays. After a relatively short period, the coloration of the superficial layer attains saturation, while that of the inner layers continues to intensify until, finally, the whole mass becomes sensibly uniform in colour.

(1) *Crystalline quartz.* The radium rays deepen the smoky appearance of the smoky quartz and transform the citrine and the rose quartz to smoky. The same effect is also observed in specimens of which the natural colours have previously been eliminated by heat treatment, while in the case of natural colourless quartz the coloration is generally not strong and lacks homogeneity.

(2) *Vitreous quartz.* Vitreous quartz specimens prepared from crystals of the different varieties are transparent and colourless. The radium rays give a violet colour to these vitreous bodies, instead of smoky. The maximum possible degree of coloration differs with the variety of quartz. In general, the effect is much more prominent in coloured quartz than in the colourless. The coloration in the latter is often irregular; in most cases the coloured and the unaffected parts are separated by a sharp boundary.

(b) *Decoloration*

The natural colours and those produced by the radium rays in quartz, both crystalline and vitreous, can be eliminated more or less easily by heating. The artificial smoky and violet tints fade with a perceptible rapidity at 190° c. and 300° c. respectively, and very rapidly at 400° c. Natural smoky coloration is more persistent than artificial, and begins to fade at about 220° c. The citrine quartz does not lose its yellow colour until 500° c. The rose-coloured quartz is the most persistent of all; complete decoloration cannot be attained below 700° c.

After the colorations produced by the radium rays have been eliminated by heating, the specimens regain their original transparency and they can be coloured again. Apparently the effect is reversible and without fatigue.

It is interesting to point out that the naturally coloured crystals of quartz, after having been blackened by the radium rays, may have their original colours completely restored by a suitable heat treatment. This fact indicates that the radium rays do not actually destroy natural colours, but that these are simply masked by superimposed smokiness.

(c) *Thermophosphorescence*

The varieties of quartz under investigation do not originally possess the property of emitting light on heating. However, under the action of radium rays they readily acquire the property of exhibiting thermophosphorescence. Crystalline rose quartz emits orange light at high temperatures, and its vitreous state gives bluish-green light. Both the crystalline and vitreous specimens of the other varieties emit either bluish-green or bluish-white light.

The specimens of quartz which have been well excited by radium rays phosphoresce brilliantly at high temperatures. It may be emphasized that thermophosphorescence and the artificial colours do not disappear simultaneously during heating. For example, at 400° c. the former lasts generally some ten minutes, while the latter disappears often in the first minutes of heating. Because of this difference in persistence, it is possible to eliminate coloration without completely destroying thermophosphorescence. The time required for the decoloration depends greatly on the temperature and also on the nature of the colour. If a strongly coloured specimen of vitreous quartz is heated at 270° c. instead of at 400° c., it is necessary to prolong the heating from the order of one minute to about two hundred hours for the removal of the violet coloration. In spite of such prolonged heating, it was found that after the heat treatment there remains always a notable proportion of thermophosphorescence. Some observations performed at 200° show that the violet fused quartz loses neither its colour nor its emissive power of phosphorescence even after a heating of ten days, and that, on the other hand, the artificial smoky specimen loses its coloration in several hours, although its thermophosphorescence does not appear to be modified sensibly. The above facts seem to be important, since it is generally believed that the coloration and the thermophosphorescence of a substance disappear simultaneously during heating. This question will be brought up again and discussed later in this paper.

(d) *Fluorescence*

Specimens of all four varieties of quartz fluoresce more or less strongly when they are exposed to the β and γ rays of radium. The fluorescence is either bluish green or bluish white in colour, except that from the crystalline rose quartz, which emits an orange light, as in the case of thermophosphorescence. In general, the fluorescence of quartz is stronger in intensity for the vitreous than for the crystalline state.

(e) *Effects produced by x rays and ultra-violet radiations*

Studies of the colouring and luminescence produced in quartz by radium rays have led the writer to examine briefly the cases when x rays and ultra-violet radiations are employed.

It was found that coloration and luminescence caused by x rays are in every respect similar to those caused by β and γ rays.

The effect of coloration produced by ultra-violet radiation is different from that produced by radium rays and x rays. Thus crystals of smoky quartz are rendered brownish but not smoky. With the specific type of hydrogen tube used, a period of exposure of the order of thirty hours is necessary for this colour to be perceptible, while no coloration was observed, for the same duration of irradiation, in the case of vitreous smoky quartz and the crystalline and vitreous specimens of other varieties.

In the course of the experiments on coloration of quartz by ultra-violet radiation, an interesting phenomenon was observed, viz., that these radiations are capable of removing the smoky colour caused by radium rays. The effect appears to be fairly strong, since an irradiation of only thirty to forty minutes

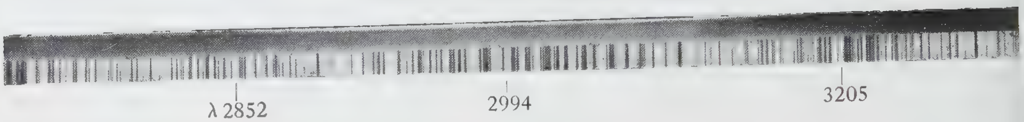

Figure 1. Absorption band of violet fused quartz.

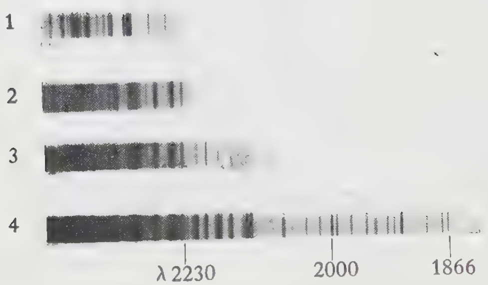

Figure 2. Spark spectra of silver, showing the limits of transparency for the crystals of the varieties: (1) rose, (2) yellow, (3) smoky, (4) colourless.

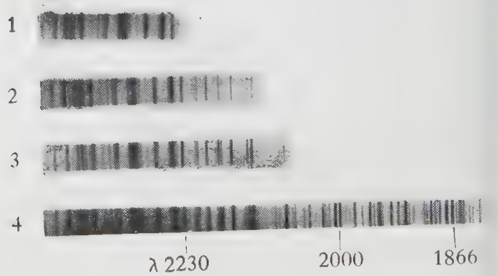

Figure 3. Spectra of silver, showing the lin of transparency for the vitreous quartz the varieties: (1) rose, (2) yellow, (3) smo (4) colourless.

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is sufficient to eliminate the colour. On the violet colour produced by radium rays in vitreous quartz, ultra-violet radiations show no perceptible effect.

The thermophosphorescence caused by the ultra-violet radiations is essentially the same as that due to radium rays. Apparently fused quartz acquires equally well the property of thermophosphorescence whether it is placed under the radiations which come through the quartz window of the hydrogen tube or from the fluorite window, whereas in the case of crystalline quartz this is no longer true; thermophosphorescence can be produced only by the radiations which pass through the fluorite window. This fact indicates that for the crystalline quartz the effect of thermophosphorescence is due to the ultra-violet radiations of wave-lengths inferior to 1850 A.

(f) *Spectroscopic properties*

(1) *Absorption spectra of coloured quartz.* The absorption spectra of coloured quartz have been studied in the visible and ultra-violet regions. For specimens of naturally coloured quartz and those rendered smoky by radium rays, such spectra show no band structure in the regions of interest. The fused quartz coloured violet by radium or X rays was found to be the only specimen with an absorption band. This band, which, so far as the writer knows, has not been observed before, is situated in the interval between $\lambda = 2750$ and $\lambda = 3200$, with maximum absorption at about $\lambda = 3000$ A., as shown in the plate, figure 1.

(2) *Transparency limits of the decolourized quartz.* In connexion with the absorption spectra of coloured quartz it may be interesting to compare the ultra-violet transparency (or rather the limit of transparency) of the decolourized specimens of coloured varieties with that of naturally colourless quartz. Such a comparison has been made for specimens in crystalline as well as in vitreous states. Corresponding crystalline and vitreous specimens were taken from the same pieces of quartz in order to avoid difference in the quantities of impurities. The specimens employed were all 1 cm. in thickness. Figures 2 and 3 represent the spectrograms for the specimens in crystalline and vitreous states respectively.

It can be seen from the above figures that the decolourized specimens of the coloured varieties are much less transparent than colourless quartz in the ultra-violet region of short wave-lengths. In passing from the naturally colourless quartz to the decolourized quartz of the different varieties, the limits of transparency receded from $\lambda = 1850$ to the vicinity of $\lambda = 2250$. Among the decolourized specimens, smoky quartz is the most transparent and rose the least. Evidently the limit of transparency varies with the quantity of impurities; consequently it will differ from sample to sample for a given variety. The values indicated in the above figures, representing the limit of transparency of some particular samples, simply give orders of magnitude.

§ 4. DISCUSSION OF RESULTS

The preceding investigations permit us to recognize some regularities and some anomalies concerning the coloration and luminescence produced by certain kinds of radiations in the different varieties of quartz. Equally they permit us to draw some conclusions as to the agencies which give rise to the coloration of quartz. With these experimental facts it is possible to clear up certain

problems regarding the nature of coloration and luminescence produced by ionizing rays and to the connexion between the phenomena of coloration and of thermophosphorescence.

E. F. Holden (1925) has compared the colour of the smoky quartz of natural origin with that produced in the laboratory by radium rays. According to him, there is a possibility that the coloration of the smoky quartz is due to the atoms of silicon, liberated under the action of the rays of radioactive substances during long geological epochs. This consideration appears to be improbable for the reason that the smoky colour produced in the laboratory is incontestably less persistent, both under heat treatment and under exposure to ultra-violet radiations, than natural smoky coloration. The facts that the crystalline and the vitreous colourless quartz are generally much lighter coloured than other varieties, and that there are often some specimens which do not allow themselves to be influenced at all by the ionizing rays, appear to indicate that neither the artificial smoky colour nor the artificial violet colour of the vitreous quartz can be attributed to the atoms or ions of silicon. J. Hoffmann (1931) referred the violet colour of the vitreous quartz to ferrous and ferric ions in the presence of titanium or zirconium. According to this author it is unlikely that the colour of the fused quartz is due to the ions or atoms of manganese, although the soda-calcic glasses, which contain some manganese, also become violet when irradiated by radium rays. It may be mentioned that the characteristic absorption band of the violet fused quartz is unfortunately found in the ultra-violet absorption region of the glasses in question; otherwise it would be possible to decide by spectroscopic method, without ambiguity, whether the absorbing agents in the glasses and in the fused quartz are different in nature.

Lind and Bardwell (1923) have described briefly their observation on the fluorescence of quartz. According to them, quartz does not fluoresce under radium rays. However, the writer has not been able to confirm this result; for, without exception, all the specimens of quartz examined fluoresce more or less strongly when they are irradiated by the β and γ rays of radium.

In comparing the spectrograms for any one variety of quartz in figures 2 and 3, it is seen that the crystals are generally somewhat more transparent than the vitreous material, and that this difference in transparency is exceptionally pronounced in the case of yellow quartz. A slight variation in transparency arising from the change in the physical state appears to be imputable to the effect of molecular scattering, which, as we know, is somewhat stronger in the vitreous than in the crystalline state. However, the unusually large variation of transparency of the yellow quartz seems to indicate that the nature of the absorbing impurities has been fundamentally modified by the change of state.

It has long been known that the ionizing rays can produce the effects of coloration and thermophosphorescence in many minerals, salts and glasses. Since these two phenomena are frequently coexistent and disappear simultaneously during heating, it would be quite natural to suppose a common basis. The theory of internal photoelectric effect has been generally adopted. According to this theory, certain electrons of the molecules which absorb the energy of the ionizing rays are displaced to some metastable levels, where they produce (or sometimes may not produce) a coloration. Their return to the

normal levels, following, for instance, a thermal agitation, involves an emission of the phosphorescence and loss of coloration. Obviously this theory associates the phenomenon of coloration with that of thermophosphorescence. However, it has been pointed out by S. C. Lind (1920) that this theory is not always true. He gave as examples the cases of certain glasses and of fused quartz. According to him, the violet colour produced in these two substances by the radium rays does not disappear below 500° C., and on the other hand, their thermophosphorescence can be eliminated at 200° C. The observations of Lind on fused quartz are evidently in contradiction to the results of the present investigation, since it is the thermophosphorescence of quartz, and not the coloration, which is more persistent.

This inconsistency in observation induced the writer to make a careful comparison of the thermophosphorescence and the decolourization due to heating violet fused quartz and violet glass, both having been coloured by radium rays. The results are summed up as follows:—(1) Under the same experimental conditions, thermophosphorescence of vitreous quartz is incontestably stronger in intensity than that of glass. (2) In conformity with the result of Lind, thermophosphorescence of glass disappears rapidly at 200° C., but its violet colour remains practically unchanged. In the case of fused quartz, as mentioned above, neither its violet colour nor its thermophosphorescence is sensibly modified at this temperature; (3) violet glass begins to decolourize at 350° C., a temperature some 150° lower than that found by Lind. On heating the violet fused quartz at 270° C. for some two hundred hours, its colour is completely eliminated, but it still shows notable thermophosphorescence. These observations certainly disclose an essential difference between the properties of violet fused quartz and those of violet glass in respect of thermophosphorescence and of thermal decoloration.

ACKNOWLEDGMENTS

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THE POLARIZING ANGLE FOR REFLECTION AT THE BOUNDARY BETWEEN TWO ABSORBING MEDIA

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ABSTRACT. The condition for the absence of a reflected wave when a plane (inhomogenous) electromagnetic wave is incident upon the plane boundary between two absorbing media is

$$\cot \phi_1 \cot \psi_2 + \cot \psi_1 \cot \phi_2 = 2,$$

ϕ_s, ψ_s being the angles that the planes of equal phase and the planes of equal amplitude respectively make with the boundary.

For small values of the conductivities no reflection is obtained at the following angles:

$$\tan \phi_1 = \sqrt{E}, \qquad \tan \phi_2 = \frac{1}{\sqrt{E}},$$

$$\tan \psi_1 = \frac{1+E\dfrac{\eta_1}{\eta_2}}{\sqrt{E}\left[\left(2+\dfrac{1}{E}\right)\dfrac{\eta_1}{\eta_2}-1\right]},$$

$$\tan \psi_2 = \frac{1+E\dfrac{\eta_1}{\eta_2}}{\sqrt{E}\left(E+2-\dfrac{\eta_1}{\eta_2}\right)},$$

where

$$E = \frac{\epsilon_2}{\epsilon_1}; \quad \eta_1 = \frac{\sigma_1}{\omega\epsilon_1}; \quad \eta_2 = \frac{\sigma_2}{\omega\epsilon_2}$$

and ϵ is the dielectric constant, σ the conductivity, and ω is $2\pi \times$ frequency.

§ 1. INTRODUCTION

The problem of determining theoretically under what conditions there is no reflected wave when a plane electro-magnetic wave is incident upon the plane boundary between two different media is a well-known one.* However, the analogue of Brewster's formula in the case of absorbing media has not, to my knowledge, been given explicitly. It is the purpose of this paper to establish it.

It is possible that the theoretical results obtained may have practical applications: dielectric constants and conductivities could be determined by measuring the angles at which no reflection occurs, in the same way as refractive indices of perfect dielectrics are found by measuring the Brewster angle.

* See, for example, J. A. Stratton, *Electromagnetic Theory* (McGraw-Hill Book Co., 1941), p. 516; J. C. Slater, *Microwave Transmission* (McGraw-Hill Book Co., 1942), p. 117; or W. König, *Handbuch der Physik*, Bd. xx (Springer, 1928), p. 194.

§ 2. FOUNDATION OF THE EQUATIONS

We take the boundary of the two media as the plane yz. We assume the electric vector of the waves to be parallel to xz, the plane of incidence, as this is the case in which we expect the reflected wave to be absent; we indicate by ϵ_1, σ_1 the dielectric constant and the conductivity of the first medium, and by ϵ_2, σ_2 those of the second; we assume the magnetic permeability of both media to be that of empty space. We indicate by A_s, B_s $(s=1,2)$ the real and imaginary parts of the propagation constants in the two media; by ϕ_1 the angle of incidence, namely, the angle that the normal to the planes of equal phase in the first medium makes with the positive x-axis; by ϕ_2 the similarly defined angle of refraction; and by ψ_1, ψ_2 the angles that the normals to the plane of equal amplitude make with the x-axis in the two media.

In absorbing media, the planes of equal phase and the planes of equal amplitude do not in general coincide, i.e., the waves are inhomogeneous, and the introduction of ψ_1, ψ_2, as well as ϕ_1, ϕ_2, is necessary. Our wave will thus be represented by

$$e^{-A_s\cos\psi_s x - A_s\sin\psi_s z - i(B_s\cos\phi_s x + B_s\sin\phi_s z) + i\omega t} \quad (s=1,2), \qquad \ldots\ldots(1)$$

where $\omega = 2\pi \times$ frequency.

Such waves can be generated in several ways: the simplest is by refraction from air to an absorbing dielectric. Waves in hollow pipes filled with an absorbing medium, and all kinds of cylindrical and spherical waves, can be represented by the superposition of inhomogeneous plane waves.

Even in perfect dielectrics the angles ϕ, ψ may be different, as, for instance, in the field in the second medium, when total reflection takes place. In this case, the planes of equal amplitude are at right angles to those of equal phase.

In this discussion, rationalized M.K.S. units are used.

The quantities in equation (1) are connected by various relations. Firstly, by the formulae defining A_s, B_s, viz.

$$\left.\begin{aligned} B_s^2 - A_s^2 &= \epsilon_s\,\mu\omega^2, \\ \text{and} \qquad 2A_sB_s\cos(\psi_s-\phi_s) &= \mu\sigma_s\,\omega; \end{aligned}\right\} \qquad \ldots\ldots(2)$$

secondly, by the law of refraction,

$$\left.\begin{aligned} B_1\sin\phi_1 &= B_2\sin\phi_2, \\ \text{and} \qquad A_1\sin\psi_1 &= A_2\sin\psi_2; \end{aligned}\right\} \qquad \ldots\ldots(3)$$

and finally by the conditions for the absence of the reflected wave; these are given by Stratton (l.c. p. 517, eq. (3)), and, using our notation, can be written

$$\left.\begin{aligned} B_1B_2\cos(\phi_1+\phi_2) &= A_1A_2\cos(\psi_1+\psi_2), \\ A_1B_2\cos(\psi_1+\phi_2) &= -A_2B_1\cos(\phi_1+\psi_2). \end{aligned}\right\} \qquad \ldots\ldots(4)$$

If we multiply A_s^2, B_s^2, σ_s and $\omega\ _\sigma$, by the same constant factor, the angles remain unchanged; it is then convenient to introduce the following dimensionless ratios:

$$E = \frac{\epsilon_2}{\epsilon_1}; \quad \eta_1 = \frac{\sigma_1}{\omega\epsilon_1}; \quad \eta_2 = \frac{\sigma_2}{\omega\epsilon_2}, \qquad \ldots\ldots(5)$$

$$\alpha_1 = \frac{A_1}{B_1}; \quad \alpha_2 = \frac{A_2}{B_2}; \qquad \beta = \frac{B_2}{B_1}. \qquad \ldots\ldots(6)$$

Equations (2), (3) and (4) then become:

$$\left.\begin{aligned} &\eta_s=\frac{2\alpha_s\cos(\psi_s-\phi_s)}{1-\alpha_s^2}; \qquad E=\beta^2\frac{1-\alpha_2^2}{1-\alpha_1^2};\\ &\beta=\frac{\sin\phi_1}{\sin\phi_2}; \qquad \frac{\alpha_2}{\alpha_1}=\frac{\sin\phi_2}{\sin\phi_1}\frac{\sin\psi_1}{\sin\psi_2};\\ &\cos(\phi_1+\phi_2)=\alpha_1\alpha_2\cos(\psi_1+\psi_2);\\ &\alpha_1\cos(\psi_1+\phi_2)=-\alpha_2\cos(\phi_1+\psi_2). \end{aligned}\right\} \qquad \text{......(7)}$$

η_1, η_2, E and β are necessarily positive quantities. If, in addition, we want the amplitude of the waves to decrease in the direction of propagation, which is the physically important case,* we must have

$$\alpha_s\cos(\psi_s-\phi_s)>0.$$

Also, of course,

$$|\alpha_1|,\ |\alpha_2|<1.$$

§ 3. CONDITIONS FOR ABSENCE OF REFLECTION

We have seven equations connecting ten quantities. Usually the constants of the two media, namely E, η_1, η_2, will be given, and we shall want to find at what angles there is no reflected wave. Conversely we can ask for what media we find no reflection at given angles. It appears immediately from the last three of equations (7) that the four angles cannot all be given arbitrarily: eliminating α_1, α_2, we find that the following relation must be satisfied:

$$\cot\phi_1\cot\psi_2+\cot\psi_1\cot\phi_2=2. \qquad \text{......(8)}$$

This, for absorbing media, is the analogue of Brewster's condition. (For $\eta_1=\eta_2=0$ we have $\psi_1=\phi_1$, $\psi_2=\phi_2$, and (8) becomes $\cot\phi_1\cot\phi_2=1$, the usual condition.)

Even subject to (8), the physically possible values of the angles are further restricted. Each of them can take any value between $-\pi/2$ and $+\pi/2$, but it is easily seen from (7), (8) that ϕ_1 and ϕ_2 must have the same sign, and we shall take them as positive; then ψ_1 and ψ_2 cannot be both negative, because this would contradict (8). We must therefore have either all four angles positive, or three positive and one of the ψ_s negative. In this last case, the corresponding α_s is negative, so that $\cos(\psi_s-\phi_s)$ must be negative, to satisfy the condition $\alpha_s\cos(\psi_s-\phi_s)>0$. The sign of α_s is immaterial when $\cos(\psi_s-\phi_s)=0$; then, unless $|\alpha_s|=1$, the corresponding medium must be a perfect dielectric, because of the first of equations (7); this case has been treated by Stratton (see later).

Solving the last three equations (7), we find:

$$\left.\begin{aligned} \alpha_1^2&=\frac{\sin\phi_1\sin\psi_2}{\sin\psi_1\sin\phi_2}\frac{\cos(\phi_1+\phi_2)}{\cos(\psi_1+\psi_2)};\\ \alpha_2^2&=\frac{\sin\psi_1\sin\phi_2}{\sin\phi_1\sin\psi_2}\frac{\cos(\phi_1+\phi_2)}{\cos(\psi_1+\psi_2)}, \end{aligned}\right\} \qquad \text{......(9)}$$

and the angles must thus be restricted to such values as make these two quantities positive and less than unity.

* Stratton, l.c., chooses instead to make the amplitude of the waves vanish at infinity.

The case $\alpha_1=\alpha_2=1$ corresponds to $\eta_1=\eta_2$, in which case $\psi_1=\phi_1$ and $\psi_2=\phi_2$ (see later).

When the above conditions are satisfied, the equations (7) can be easily solved, and the values of E, η_1, η_2 found.

§ 4. PARTICULAR CASES

Reverting to the usual case, the equations (7) can be solved for given E, η_1, η_2, but, as with the equivalent equations given by Stratton, no simple expressions can be obtained for the angles.

The solution, however, is easily obtained in limiting cases, to which we shall confine ourselves.

(a) $\eta_1, \eta_2 \ll 1$

Keeping only quadratic terms in η_1, η_2, we have

$$\left.\begin{aligned}
\tan\phi_1 &= \sqrt{E}\left[1+(\eta_2-\eta_1)\frac{(1-E)\eta_1+(3E+1)\eta_2}{8(E+1)}\right],\\
\tan\phi_2 &= \frac{1}{\sqrt{E}}\left[1+(\eta_2-\eta_1)\frac{(E+3)\eta_1+(E-1)\eta_2}{8(E+1)}\right],\\
\tan\psi_1 &= \sqrt{E}\,\frac{\eta_2+E\eta_1}{(2E+1)\eta_1-E\eta_2},\\
\tan\psi_2 &= \frac{1}{\sqrt{E}}\,\frac{\eta_2+E\eta_1}{(E+2)\eta_2-\eta_1}.
\end{aligned}\right\} \qquad \ldots\ldots(10)$$

ψ_1, ψ_2 depend thus only on the ratio $\eta_1/\eta_2=\epsilon_2\sigma_1/\epsilon_1\sigma_2$. The values of $\tan\psi_1$ and $\tan\psi_2$ for different values of this ratio are given in the following table:—

η_1/η_2	$\tan\psi_1$	$\tan\psi_2$
0	$-1/\sqrt{E}$	$1/\sqrt{E}(E+2)$
$E/(2E+1)$	$\mp\infty$	$1/2\sqrt{E}$
1	$\sqrt{E}$	$1/\sqrt{E}$
$E+2$	$\sqrt{E}/2$	$\pm\infty$
∞	$E\sqrt{E}/(2E+1)$	$-\sqrt{E}$

When η_1, η_2 increase, so that the above approximation is no longer valid, ψ_1, ψ_2 depend on the actual values of η, η_2 and not only on their ratio. The angles, however, vary much, as they do for η_1, η_2 small.

(b) $\eta_1, \eta_2 \gg 1$

We have

$$\left.\begin{aligned}
\tan\phi_1 &= \sqrt{\frac{E\eta_2}{\eta_1}}\left[1-\frac{\eta_2-\eta_1}{2\eta_1\eta_2}\right],\\
\tan\phi_2 &= \sqrt{\frac{\eta_1}{E\eta_2}}\left[1+\frac{\eta_2-\eta_1}{2\eta_1\eta_2}\right],\\
\tan\psi_1 &= \sqrt{\frac{E\eta_2}{\eta_1}}\left[1+\frac{\eta_2-\eta_1}{2\eta_1\eta_2}\right],\\
\tan\psi_2 &= \sqrt{\frac{\eta_1}{E\eta_2}}\left[1-\frac{\eta_2-\eta_1}{2\eta_1\eta_2}\right].
\end{aligned}\right\} \qquad \ldots\ldots(11)$$

Thus in this case all four angles are positive, and ψ_s and ϕ_s differ only by terms in η^{-1}. In this approximation also the angles depend only on the ratio η_1/η_2.

(c) *Medium* (1) *is a dielectric and medium* (2) *is a conductor*

This is the case treated by Stratton (l.c. p. 520). Of course, if medium (1) is a perfect dielectric, the incident wave must have the planes of equal phase perpendicular to the planes of equal amplitude.

(d) $\eta_1 = \eta_2$ *and of unrestricted magnitude*

In this case

$$\left.\begin{aligned} \tan\psi_1 &= \tan\phi_1 = \sqrt{E}, \\ \tan\psi_2 &= \tan\phi_2 = 1/\sqrt{E}. \end{aligned}\right\} \qquad \ldots\ldots (12)$$

Thus, when $\eta_2 = \eta_1(\epsilon_1\sigma_2 = \epsilon_2\sigma_1)$, no reflection is obtained with planes of equal phase coincident with planes of equal amplitude and at the Brewster angle.

(e) $\psi_1 = \psi_2 = 0$

As appears immediately from (7), (8), it is impossible for the reflected wave to be absent if $\psi_1 = \psi_2 = 0$; this is the case for the component (criss-cross) waves in hollow tubes, when the boundary between the two media is at right angles to the axis of the tube.

RECTANGULAR VOLTAGE WAVES FROM A LOW IMPEDANCE SOURCE

By T. J. REHFISCH,
Northampton Polytechnic
(Now at Electrical Research Association)

Demonstrated 27 *October* 1944

§ 1. INTRODUCTION

THE response of a physical system to a suddenly applied force has received much attention, electrical networks and Heaviside's Unit Function being of particular interest today.

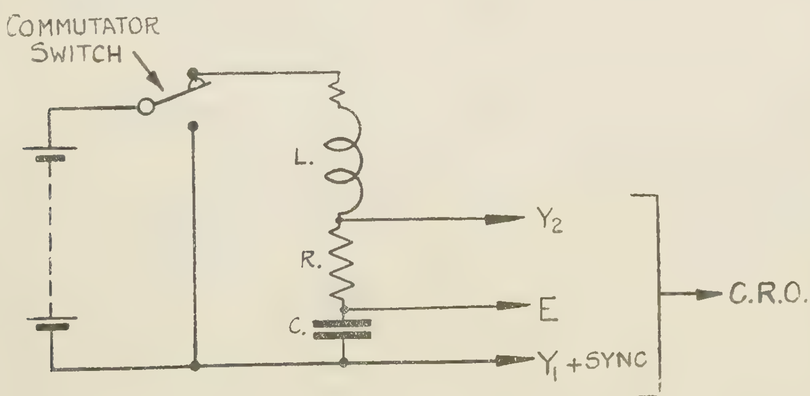
Experimental difficulties attaching to such "single transient" phenomena may, for some purposes, be overcome by periodic repetition of the transient, i.e. by the generation of a rectangular wave and its application to the test circuit; providing that the circuit reaches the steady state within the half-period of the wave, the transient behaviour of the circuit will be repeated over and over again and may be examined on an oscilloscope.

"Square-wave" generators using thermionic valves have been used extensively in recent times; however, there are reasons why a reversion to a mechanical "make-and-short" device is advantageous for demonstrations or even for work on scale models; primarily, because the internal impedance of this form of

generator is very small, being composed mainly of battery and brush-commutator contact resistances—a residual few ohms at most; this compares with many and unsteady thousands of ohms contributed by alternative low-power (thermionic) generators. Hence the mechanical device allows many circuit phenomena to be observed on a reduced frequency scale—in particular, oscillatory phenomena, which, with a high-impedance generator, occur in the radio-frequency range, may easily be obtained at moderate audio frequencies. Ordinary variable standard components—resistors, self- and mutual inductors, capacitors—may be readily used; their stray parameters, vitiating at radio frequencies, being of little importance in these experiments (with the exception of coil self-capacity), known and controllable changes in circuit parameters are readily achieved. Moreover, the low residual internal impedance of the mechanical generator may be increased at will by adding resistance externally; finally, by a simple re-connection, the "internal resistance" may be made different during the application of the p.d., and its removal, respectively. As an extreme case, a "make-and-break" arrangement leaves the circuit open whenever the battery is removed.

§ 2. APPARATUS

The generator consists of a battery feeding a motor-driven "Fleming-Clinton commutator", modified by the addition of another centre brush; the two centre brushes are normally joined electrically and spaced accurately to ensure equal make-and-break periods and leave no observable insulating interval, without shortening the battery excessively.* The battery is connected between the outer brushes, and the output is taken from one of these and the centre pair.



Circuit for investigation of *L–C–R* (series) circuit.

A commercial double-beam oscillograph is connected to the test circuits, one beam normally showing the p.d. wave-form existing across the condenser in the primary circuit, the second beam revealing the p.d. wave-form across a resistor in the primary circuit (current wave-form), or across a condenser in the secondary circuit. The time base of the C.R.O. is locked to the repetition rate of the generator (60 c.p.s.), or half this value, as the case may be.

* A paraffin lubricant was found essential for good contacts.

§ 3. OBSERVATIONS

Observations carried out with the equipment, some of which were demonstrated to the Society, are summarized in the following table, which shows the circuit and the parameters which can usefully be varied, with notes on the effects thus illustrated.

Circuit	Variable parameters	Observations of particular interest
A. Any	C.R.O. time base	Rectangular wave output unaffected by test circuit.
	B.F.O. output	Comparison with B.F.O. sine-wave.
B. C–R in series	C, R	Condenser p.d. and its differential C/t, resistance p.d. (current). Rate of rise depends on $1/CR$; crest value of p.d.s unaffected by (CR) value, providing sufficient time is allowed.
C. L–C–R in series (LC) small	L, C, R	Introduction of L speeds up attainment of steady state. Critical damping. Verification of condition $\frac{1}{LC}-\frac{R^2}{4C^2}=0$. Overshooting; damped oscillations of period determined by LC. Damping factor $R/2L$ independent of C.
D. L–C–R in series, (LC) large	C, R	Condenser p.d. overshoot limited to $< 2E$. When $2\pi\sqrt{LC}=T$ (repetition period), the circuit may be tuned to the applied wave (the fundamental and the second harmonic components). Condenser p.d. " purer " than current. Coil p.d. very discontinuous.
E. L–C–R_2 in parallel, R_1 in series Make and short	R_2, L, C	Observations appear as duals of (D), but the current first " undershoots ". Damping by R_2 leads to single-pulse p.d. ; its width is shortened by decreasing L, C, increasing R_2 ; its height limited by E.
Make and break		On open-circuiting the circuit wherein the coil carries a steady current, damped oscillations are produced ; a 2-v. battery energizes it sufficiently to produce oscillations filling the screen (100-v. peak to peak). Their period depends on LC, their initial value on $\frac{1}{R_1}\sqrt{\frac{L}{C}}$, their damping on $1/R_2$ and C, but not on L. At critical damping, a single pulse is generated.
Rectifier connected across the parallel circuit Neon lamp connected across circuit		This suppresses the oscillation completely, or leaves the first half-cycle only, according to the sense of connexion.

Circuit	Variable parameters	Observations of particular interest
F. Coupled circuits		
Both coils aperiodic	M	Make: rise of primary p.d. depends on M; non-oscillatory secondary current, direction determined by sign of M. Short: oscillatory fall of p.d.
Primary coil tuned	R_2	Damping of primary coil increased by reducing R_2.
Both coils tuned	M	Circuits isochronous: as M is increased, the damped oscillations in the primary circuit are broken up into separate packets, eventually too close to be distinguished; the envelopes of corresponding secondary circuit oscillations are in antiphase to the envelope of the primary. "Turn-over" points.
	C_2	At 20% coupling, a maximum secondary oscillation occurs when the circuits are isochronous; smaller C_2 values effect substantial and more rapid secondary oscillations, while with C_2 some four or more times larger, the secondary condenser p.d. falls to practically zero, and the effect is similar to a short circuit on C_2.
Secondary circuits also connected to source	M	Type of oscillation depends on mode of excitation—beats are suppressed, frequency determined by sign of M.

DISCUSSION

on papers by L. S. GODDARD (*Proc. Phys. Soc.*, **56**, 372 (1944)) and L. S. GODDARD and O. KLEMPERER (*ibid.* **56**, 378 (1944)) on Electron microscopes.

Dr. L. J. COMRIE. I approve very much of this "back to nature" movement, in which the fundamental equations are treated rigorously, and I admire anyone who has the courage to face the necessary arithmetic. Perhaps the classical instance of this principle is Cowell's work on Halley's comet. Up to this time an elliptical orbit was used as a first approximation, and perturbations due to the major planets were applied. In this process, second-order terms, due to the difference between the assumed and the true position of the comet, eventually become burdensome. Cowell therefore discarded the elliptical orbit, and combined all attractions, *including that of the Sun*, in his step-by-step solution of the equations of motion. His success in predicting the return to perihelion to within two days over a period of 75 years (equivalent to 5-figure accuracy) is ample testimony to his treatment.

The W. E. Milne step-by-step method of numerical integration, as used by Mr. Goddard, is described in a series of pamphlets issued by the Marchant Calculating Machine Company, of which I am expecting a supply soon for distribution. My first examination of the method failed to convert me from the usual finite difference methods, especially those in which the computer estimates one or more higher-order differences of the highest differential and then produces (usually in pencil) enough central differences to use central-difference formulae to get values of the integral that suffice for use in the differential equation. The values of the differential obtained by substitution in the equation are

then compared with the estimated values. Although this is theoretically an iteration process, in practice a good computer will not need repetitions. I can speak from experience, as 14 of my girls, whose average age is less than 21, have just spent several months solving pairs of simultaneous differential equations of the second order.

The lack of attractiveness here is similar to that in the Lagrangian formula for interpolation and is due to (1) the loss of the sheet anchor of the differences, which not only detect errors, but also guide us to any necessary changes of interval ; (2) the fact that the method is " blind " and cannot see how many function values to use, or detect errors in them easily. That such methods are more attractive with a machine like the latest electric Marchant is true, but I cannot resist the feeling that the method is here the slave of the machine, instead of the converse.

Mr. T. Smith. I think the outstanding fact which emerges from these papers is that a method of calculation has been evolved which is quick, well-adapted to existing machines, and gives results in good agreement with experiment. From the description it appears that the method can be safely applied by computers who are by no means trained mathematicians. I am glad to see a method of this kind established, for it has seemed to me inappropriate to expect methods developed for glass optics * to be suitable for electron optical problems. The distinction between the abrupt changes characteristic of the one system and the continuous changes of the other appeared so important that I have not regarded very seriously any work on electron optics done by the usual optical methods. The one optical method which should undoubtedly be appropriate is that of the characteristic function, and I hope to discuss this some time with Mr. Goddard. As this method may be regarded indifferently as optical or dynamical—it is, in fact, the origin of Hamilton's equations of motion—there is no doubt that it has a strong *prima facie* claim to consideration.

Dr. W. D. Wright. Greater accuracy in the tracing of electron paths is obviously to be desired, and it would seem that Mr. Goddard's method represents an important advance over previous attempts. There may still, however, be a useful field of application for more approximate calculations, since the tracing of an electron through a particular lens is rarely undertaken because of any inherent interest in the path itself, but rather as a means to improving the design of a lens in respect of its aberrations. In the method adopted by Dr. Klemperer and myself, to which Mr. Goddard has referred, we sub-divided the system into a number of refracting surfaces and endeavoured to calculate the contributions which each surface made to the final aberration, by means of optical formulae developed by Conrady. When these contributions are known, it is possible to visualize the changes required in the refracting surfaces, that is, in the electrostatic field, in order to improve the aberrations. The fact that the data are only approximate is not really important, so long as the direction in which the aberrations will change with a given change in shape of the refracting surfaces can be deduced. I am not clear that the equivalent information can be obtained from an accurate method of ray tracing in which the field is treated as continuously variable, and it is certainly not possible to take advantage of the mass of information and experience accumulated in the design of glass lens systems. Our method was especially successful in providing a simple derivation of the Petzval curvature of field and in comparing the problem of flattening the field of an electron lens with that of designing an anastigmatic photographic lens.

Authors' reply. Dr. Comrie's suggestion that a method using differences may be preferable to one using ordinates only is certainly worthy of consideration. As stated in the first paper, each method was tried and the method using ordinates proved to be much quicker, and so was adopted. But this was the sole reason, and we agree that the method using differences is safer, and in some problems it may actually be more rapid. If, for example, the conditions of the field or the electron change a great deal over the portion

* It is often forgotten that the current trigonometric methods of lens design were adopted, not because they were, without qualification, the best for the purpose, but because, taking into consideration tabular and other aids to calculation available at the time, they were considered the methods most suitable for application by workers merely trained as routine computers. Apart from vested interests of one kind and another, I think they have little claim to serious consideration today. What is important is the accumulated knowledge that has been gained by their use, and this in different circumstances would have been obtained in other ways.

of the path to be determined, then the problem of a change of interval may arise. In this case the method recommended by Dr. Comrie might well prove to be superior because it would reveal when the interval should be altered and what alteration is necessary. This problem, however, did not arise in the case of the magnetic lens.

Mr. Smith's remark about the possibility of using the method of the characteristic function is very interesting. It is also very valuable because this method, when it can be applied in practice, is one of great power, and there has been a tendency in some quarters to neglect its possibilities. The refractive index, in the electron-optical case, is given by

$$\mu(r,\mathfrak{s}) = \phi^{\frac{1}{2}} + \eta(\mathbf{A}\mathfrak{s}) = \phi^{\frac{1}{2}} + \left(\frac{e}{2m}\right)^{\frac{1}{2}}(\mathbf{A}\mathfrak{s}),$$

where ϕ and $\mathbf{A}$ are the electric and magnetic potentials respectively, and $\mathfrak{s}$ is the vector,

$$\mathfrak{s} \equiv \left(\frac{dr}{d\sigma},\ r\frac{d\psi}{d\sigma},\ \frac{dz}{d\sigma}\right),$$

obtained by differentiating along the path. From this it is evident that the medium is heterogeneous and, when a magnetic field is present, also anisotropic. This shows how inadequate it is to expect much help from the analogy of glass optics where the medium is homogeneous and isotropic. It should be stated that the method of the characteristic function, or at least an equivalent, has been studied by Glaser in a series of papers in the *Zeitschrift für Physik*. However, even Glaser does not appear to have considered the full possibilities of the method. A further study is certainly desirable, as Mr. Smith suggests.

We agree with Dr. Wright that there is seldom any intrinsic interest in the path itself, and this fact was appreciated at the time the papers were written. The problem was not so much to develop a method for very accurate ray tracing as to provide a method which was general and at the same time did not introduce the very large errors that are inherent in some of the methods used hitherto. In the case of magnetic lenses, ray-tracing proved to be impracticable for reasons pointed out in the second paper, and it was necessary to develop an alternative method. It was possible to solve this problem only by freeing oneself from the methods of ray tracing which had become standard during the last ten years or so. Only by a return to the exact equations of motion and a numerical solution of these by a method that has a rigorous mathematical derivation could one hope to achieve the desired accuracy and generality. The new method, considering the accuracy of its results, is considerably quicker (when used in conjunction with a modern calculating machine) than the methods hitherto developed. No time is lost in referring to tables of functions or in plotting or using graphs, and it is unnecessary to calculate any auxiliary quantities. The method is, in fact, an *algebraic* process.

In the case of trigonometric ray tracing, the convergence is slow, as may be seen by referring to table 1 on p. 300 of the paper by Dr. Klemperer and Dr. Wright (*Proc. Phys. Soc.* **51,** 296 (1939)). By solving numerically the equations of motion it would be possible, for a given accuracy, to use a much smaller number of points because, in passing from a point P_n to P_{n+1}, use is made of much more information than merely the conditions existing at P_n.

Regarding the estimation of lens errors, it should be noted that these may be calculated by means of formulae developed in the series of papers by Glaser, mentioned above ; and these may well prove to be of importance in the design of electron-optical systems. For this purpose it seems doubtful whether extensive use could be made of experience gained in glass optics, and on this point it is worth noting the remarks made by Mr. Smith. In glass optics the refractive index of a medium may be changed without altering that of neighbouring media, but in electron optics the system must be considered *as a whole*, and the reduction of errors will be achieved through a consideration of integral rather than differential (or local) conditions.

For the Petzval curvature an exact expression has been given in terms of the field strength (see, for example, W. Glaser, *Z. Phys.* **97,** 177 (1935), and, in particular, p. 195). We have, using Glaser's notation, $C-D$ for the Petzval curvature,

$$C-D = \tfrac{1}{8}\int_a^b \frac{\phi''(z) + 4\eta^2 H^2(z)}{\{\phi(z)\}^{\frac{1}{2}}}\,dz,$$

where $\phi(z)$ and $H(z)$ are the scalar potential and magnetic field strength along the axis. In the case of a purely electrostatic lens we have $H(z)\equiv 0$, so that

$$C-D=\tfrac{1}{8}\int_a^b \frac{\phi''(z)}{\{\phi(z)\}^{\frac{3}{2}}}\,dz.$$

This formula * gives the curvature more rapidly than that used by O. Klemperer and W. D. Wright, as only a single (numerical) integration is needed. It is also evident that the contribution of different parts of the field to the curvature may be found by studying the function $\phi''(z)/\{\phi(z)\}^{\frac{3}{2}}$. It is hoped to treat the question of aberrations of electrostatic and magnetic lenses in a future paper.

* The formula used by Dr. Wright may be easily derived from that given. The refractive index μ is given by $\mu=k\phi^{\frac{1}{2}}$, where k is constant, and the radius of curvature of the equipotentials (on the axis) is (see Myers, *Electron Optics* (London, 1939), p. 95) :

$$R=2\phi'(z)/\phi''(z).$$

Hence

$$C-D=\tfrac{1}{4}\int_a^b \frac{\phi'(z)}{R\{\phi(z)\}^{\frac{3}{2}}}\,dz=\tfrac{1}{2}k\int_a^b \frac{\mu' dz}{R\mu^2}.$$

If the integral is now replaced approximately by a sum we obtain the desired form.

CORRIGENDUM

Paper on "A mean scotopic visibility curve, by W. S. Stiles and T. Smith (*Proc. Phys. Soc.* **54**, 251 (part 4, 1944)).

The measurements of Hecht and Williams (1922) were made for binocular vision, ***not*** monocular vision as stated, and the number of observers was 48. The authors are indebted to Prof. Hecht for this additional information.

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